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Description

The present invention is directed to an ink composition containing modified pigment particles as a colorant. More specifically, the present invention is directed to an ink composition comprising a liquid vehicle and pigment particles that have been treated with a vinyl aromatic salt which has been polymerized and attached to the surfaces of the pigment particles by chemical bonding (grafting). The ink composition of the present invention is suitable for use in various applications, such as ink for writing pens, inks for conductive coatings and conductive images, and inks for printing and graphic applications. In addition, ink compositions of the present invention are particularly suitable for ink jet printing processes, including thermal ink jet printing processes, acoustic ink jet printing processes, piezoelectric ink jet and continuous ink jet printing processes.

Ink jet printing systems generally are of two types: continuous stream and drop-on-demand. In continuous stream ink jet systems, ink is emitted in a continuous stream under pressure through at least one orifice or nozzle. Multiple orifices or nozzles also can be used to increase imaging speed and throughput. The stream is ejected out of orifices and perturbed, causing it to break up into droplets at a fixed distance from the orifice. At the break-up point, the electrically charged ink droplets are passed through an applied electrode which is controlled and switched on and off in accordance with digital data signals. Charged ink droplets are passed through a controllable electric field which adjusts the trajectory of each droplet in order to direct it to either a gutter for ink deletion and recirculation or a specific location on a recording medium to create images. The image creation is controlled by electronic signals.

In drop-on-demand systems, a droplet is ejected from an orifice directly to a position on a recording medium by pressure created by, for example, a piezoelectric device, an acoustic device, or a thermal process controlled in accordance with digital data signals. An ink droplet is not generated and ejected through the nozzles of an imaging device unless it is needed to be placed on the recording medium.

Since drop-on-demand systems require no ink recovery, charging, or deflection operations, the system is simpler than the continuous stream type. There are three types of drop-on-demand ink jet systems. One type of drop-on-demand system has an ink filled channel or passageway having a nozzle on one end and a regulated piezoelectric transducer near the other end to produce pressure pulses. The relatively large size of the transducer prevents close spacing of the nozzles necessary for high resolution printing, and physical limitations of the transducer result in low ink drop velocity. Low drop velocity may seriously diminish tolerances for drop velocity variation and directionality, thus impacting the system's ability to produce high quality copies, and also decreases printing speed. Drop-on-demand systems which use piezoelectric devices to eject the ink droplets also suffer the disadvantage of a low resolution. A second type of drop-on-demand ink jet device is known as acoustic ink printing which can be operated at high frequency and high resolution. The printing utilizes a focused acoustic beam formed with a spherical lens illuminated by a plane wave of sound created by a piezoelectric transducer. The focused acoustic beam reflected from a surface exerts a pressure on the surface of the liquid, resulting in ejection of small droplets of ink onto an imaging substrate. Aqueous based inks can be used in this system.

The third type of drop-on-demand system is known as thermal ink jet, or bubble jet, and produces high velocity droplets and allows very close spacing of nozzles. The major components of this type of drop-on-demand system are an ink filled channel having a nozzle on one end and a heat generating resistor near the nozzle. Printing signals representing digital information generate an electric current pulse in a resistive layer (resistor) within each ink passageway near the orifice or nozzle, causing the ink in the immediate vicinity of the resistor to be heated up periodically. Momentary heating of the ink leads to its evaporation almost instantaneously with the creation of a bubble. The ink at the orifice is forced out of the orifice as a propelled droplet at high speed as the bubble expands. When the hydrodynamic motion of the ink stops after discontinuous heating followed by cooling, the subsequent ink emitting process is ready to start all over again. With the introduction of a droplet ejection system based upon thermally generated bubbles, commonly referred to as the "bubble jet" system, the drop-on-demand ink jet printers provide simpler, lower cost devices than their continuous stream counterparts, and yet have substantially the same high speed printing capability.

The operating sequence of the bubble jet system begins with a current pulse through the resistive layer in the ink filled channel, the resistive layer being in close proximity to the orifice or nozzle for that channel. Heat is transferred from the resistor to the ink. The ink becomes superheated far above its normal boiling point, and for water based ink, finally reaches the critical temperature for bubble nucleation and formation of around 280 °C and above. Once nucleated and expanded, the bubble or water vapor thermally isolates the ink from the heater and no further heat can be applied to the ink. This bubble expands rapidly due to pressure increase upon heating until all the heat stored in the ink in excess of the normal boiling point

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diffuses away or is used to convert liquid to vapor, which removes heat due to heat of vaporization. The expansion of the bubble forces a droplet of ink out of the nozzle located either directly above or on the side of a heater, and once the excess heat is removed with diminishing pressure, the bubble collapses on the resistor. At this point, the resistor is no longer being heated because the current pulse has been terminated and, concurrently with the bubble collapse, the droplet is propelled at a high speed in a direction towards a recording medium. Subsequently, the ink channel refills by capillary action and is ready for the next repeating thermal ink jet process. This entire bubble formation and collapse sequence occurs in about 30 microseconds. The heater can be reheated to eject ink out of the channel after 100 to 2,000 microseconds minimum dwell time and to enable the channel to be refilled with ink without causing any dynamic refilling problem. Thermal ink jet processes are well known and are described in, for example, U.S. Patent 4,601,777, U.S. Patent 4,251,824, U.S. Patent 4,410,899, U.S. Patent 4,412,224, and U.S. Patent 4,532,530.

Known ink jet ink compositions generally comprise a dye which is soluble in an ink vehicle such as water or a mixture of water and a water soluble or water miscible organic solvent. The colorant in these inks is a soluble dye rather than a pigment. Inks comprising soluble dyes can exhibit many problems, such as poor waterfastness, poor lightfastness, clogging of the jetting channels as a result of solvent evaporation and changes in the dye's solubility, dye crystallization, ink bleeding when prints are formed on plain papers, poor thermal stability, chemical instability, ease of oxidation, and low drop velocity. In addition, many of the dyes contained in inks may be potentially mutagenic. These problems can be minimized by replacing some of the dyes used in ink formulations with insoluble pigments. In general, pigments have superior properties with respect to dyes, such as good waterfastness, good lightfastness, good image density, thermal stability, oxidative stability, the ability to perform intercolor ink mixing, compatibility with both coated/treated and plain papers, and non-mutagenic properties.

Ink jet inks containing pigment particles as colorants are known. For example, in Dunn, "Waterproof Carbon Black Ink for Ink Jet Printing," Xerox Disclosure Journal, Vol. 4, No. 1 (1979), a waterproof colloidal carbon black ink for ink jet printing is disclosed. The ink is prepared by incorporating a water-resistant acrylic polymer binder into an ink jet ink, such that the ink composition comprises about 9 percent by weight of carbon black, about 2 percent by weight of an anionic polymer-type dispersing agent, about 5 percent by weight of polyethylene glycol, about 8 percent by weight of Carboset 514H, and about 76 percent by weight of ammoniated distilled water. Sufficient ammonium hydroxide is added to the ink to adjust the pH to 8.5. According to the article, this ink composition is particularly suited to ink jets run in a continuous mode.

In addition, U.S. Patent 4,597,794 discloses an ink jet recording process which comprises forming droplets of an ink and recording on an image receiving material by using the droplets, wherein the ink is prepared by dispersing fine particles of a pigment into an aqueous dispersion medium containing a polymer having both a hydrophilic and a hydrophobic construction portion. The hydrophilic portion constitutes a polymer of monomers having mainly additively polymerizable vinyl groups, into which hydrophilic construction portions such as carboxylic acid groups, sulfonic acid groups, sulfate groups, and the like are introduced. Pigment particle size may be from several microns to several hundred microns. The ink compositions disclosed may also include additives such as surfactants, salts, resins, and dyes.

U.S. Patent 3,705,043 discloses an ink suitable for jet printing which comprises a high infrared absorbing coloring component and a humectant in the form of an aliphatic polyol, alkyl ether derivatives of aliphatic polyols, and mixtures thereof in aqueous media. The infrared absorber component may be a high infrared absorptive water soluble dye, a solution of water dispersed carbon blacks, or mixtures thereof. In addition, U.S. Patent 3,687,887 discloses an ink jet ink having application onto a film base which comprises an aqueous system containing 1 to 5 percent by weight of a dissolved styrene-maleic anhydride resin, 3 to 20 percent by weight of glycol ethers, and up to 4 percent by weight of carbon black in suspension or 1 to 4 percent of orthochromatic dyes in solution, or both, plus additives such as tinting dyes. Example 1 of this patent discloses a general ink formulation containing carbon black and a glycol ether, which may be an ethylene glycol type ether. Further, Japanese Patent 59-93765 discloses a recording liquid for ink jet printers. The ink disclosed therein is designed for dissolution stability at temperatures above 250 °C to prevent damage to the ink jet head, and comprises a dye, a solvent such as water, an organic solvent, an optional surface tension controller, a viscosity controller, and other additives. An amount of C.I. Food Black 2 is used as the colorant, and is present in the liquid in an amount of 0.5 to 15 percent by weight.

U.S. Patent 4,273,847 discloses a printing ink comprising particles of small size, each having a body portion consisting of a fusible resin with a colorant dispersed therein and an electrically conductive material, which may be carbon particles, situated substantially entirely on the surface of the body portion and comprising 5 to 10 percent of the weight of the ink. The disclosed ink is suitable for use in pulsed electrical printing.

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Further, U.S. Patent 4,530,961 discloses an aqueous dispersion of carbon black grafted with hydrophilic monomers of alkali or ammonium carboxylate bearing polyacrylates, which suspension may be used for manufacturing ink jet inks. The dispersion has a viscosity of about 2 to about 30 centipoise for a carbon black content of about 1 to 15 percent by weight. This composition may also contain surfactants, wetting agents, dyes, mold inhibitors, oxygen absorbers, buffering agents, pH controlling agents, and viscosity controlling agents. Carbon black particles contained in the composition are of a size that permits them to pass easily through 1 to 50 micron mesh filters. Example 9 of this reference discloses three possible ink compositions containing the carbon black suspension. In addition, at column 1, lines 43 to 46, this patent indicates that it is known to graft hydrophobic styrene onto carbon black.

The use of aromatic sulfonates as surfactants is also known. For example, U.S. Patent 2,629,697 discloses a liquid composition comprising sodium alkyl aryl sulfonate, liquid hydrocarbon, and an aliphatic hydroxy compound, and optionally also containing water. The compound is useful as an emulsion type cleaning compound. In addition, U.S. Patent 2,335,505 discloses a typographic printing ink vehicle which comprises alkali metal silicates dissolved in mixtures of water with water-miscible organic solvents. The ink can also contain an aromatic ester sulfonate. Further, U.S. Patent 3,844,994 discloses an ink formulation useful in lithographic printing processes which is a stable emulsion comprising an oleophilic phase and a hydrophilic phase, comprising one or more polyhydric alcohols, a surfactant, and polystyrene sulfonate.

Additional references of background interest include U.S. Patent 3,846,141, U.S. Patent 4,165,399, U.S. Patent 4,409,039, U.S. Patent 4,409,040, and U.S. Patent 4,508,570.

Although known inks are suitable for their intended purposes, a need continues to exist for ink compositions containing pigment particles as colorants. In addition, a need exists for ink compositions wherein pigment particles are stably dispersed in an aqueous medium. A need also exists for ink compositions suitable for ink jet printing. Further, there is a need for ink compositions that generate high quality images on a variety of substrates, including plain and treated papers, transparencies, plastic, and fabric, when employed in ink jet printing processes, including continuous ink jet printing and drop-on-demand processes. There is also a need for ink compositions suitable for use in ink jet printing systems wherein the images generated exhibit excellent image sharpness, lightfastness, waterfastness, and optical density as well as the absence of feathering and the absence of mottling in solid image areas. Further, a need exists for ink compositions that contain conductive pigment particles, wherein images generated with the liquids are electrically conductive and enable preparation of a conductive image or pattern on a nonconductive substrate. A need also exists for ink compositions that are nontoxic and nonmutagenic. There is also a need for ink compositions suitable for ink jet printing that exhibit low viscosities of less than 0.005 Pa.s (5 centipoise). Additionally, there is a need for ink compositions containing pigment particles with an average diameter of less than 3 μm , and preferably less than 1 μm . Further, a need remains for ink compositions capable of generating images with optical density of over 1.20 on various plain papers.

It is the object of the present invention to provide an ink composition that generates high quality images on a variety of substrates when employed in ink jet printing processes, including continuous ink jet printing and drop-on-demand processes, wherein the images generated exhibit excellent image sharpness, lightfastness, waterfastness, and optical density as well as the absence of feathering and the absence of mottling in solid image areas, wherein images generated with the liquid are electrically conductive and enable preparation of a conductive image or pattern on a nonconductive substrate, which ink composition is nontoxic and nonmutagenic, exhibits a low viscosity of less than 0.005 Pa.s (5 centipoise), and which is capable of generating images with optical density of over 1.20 on various plain papers.

This object of the present invention can be achieved by an ink composition comprising an aqueous liquid vehicle and pigment particles having chemically grafted to the surfaces thereof a polymerised vinyl aromatic salt in the form of a homopolymer or a copolymer.

The polymerized vinyl aromatic salt is attached to the pigment particle surfaces by chemical bonding or grafting.

The present invention is also directed to a process for preparing an ink composition which comprises mixing in water a pigment and a vinyl aromatic salt, attriting the mixture until the pigment particles have an average particle diameter of from 0.001 to 20 μm , adding to the mixture a water soluble free radical polymerization initiator and heating the mixture under vacuum or inert atmosphere, thereby polymerizing the vinyl aromatic salt and chemically grafting it to the pigment particle surfaces, separating the pigment particles from the mixture, and admixing the pigment particles with a liquid vehicle, as well as a process for preparing an ink composition which comprises:

a. preparing modified pigment particles by:

i. first mixing together in water a free radical polymerization initiator and a monomeric vinyl aromatic salt and heating the mixture under vacuum or inert atmosphere, thereby polymerizing the vinyl

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aromatic salt; and

- ii. subsequently adding to the polymerized vinyl aromatic salt pigment particles with an average particle diameter of from 0.001 to 10 μm , additional vinyl aromatic salt monomers, and optionally free radical polymerization initiator, thereby further polymerizing the vinyl aromatic salt and resulting in chemical grafting of the polymerized vinyl aromatic salt to the surfaces of the pigment particles; and
- b. admixing the modified pigment particles thus prepared with a liquid vehicle.

Another embodiment of the present invention is directed to a process which comprises incorporating into an ink jet printing apparatus an ink composition comprising an aqueous liquid vehicle and pigment particles having chemically grafted to the surfaces thereof a polymerised vinyl aromatic salt, and causing the ink to be ejected in droplets in an imagewise pattern onto a substrate, thereby forming an image.

The ink composition of the present invention comprises modified pigment particles in a liquid vehicle. The liquid vehicle can consist solely of water, or it can comprise a mixture of water and a water soluble or water miscible organic component, such as ethylene glycol, propylene glycol, diethylene glycol, glycerine, dipropylene glycol, polyethylene glycols, polypropylene glycols, amides, ethers, carboxylic acids and their salts, esters, alcohols, organosulfides, organosulfoxides, sulfones, alcohol derivatives, hydroxyether derivatives such as butyl carbitol or cellusolve, amino alcohols, ketones, polyelectrolytes, and other water soluble or water miscible materials, as well as mixtures thereof. When mixtures of water and water soluble or miscible organic liquids are selected as the liquid vehicle, the water to organic ratio typically ranges from about 100:0 to about 40:60, and preferably from about 97:3 to about 50:50. The non-water component of the liquid vehicle generally serves as a humectant which has a boiling point higher than that of water (100°C). The liquid vehicle should permit an emulsion or a colloidal suspension of the pigment particles in the ink, and should have evaporation characteristics allowing for the desired ink jet printing speed if the ink is to be used in an ink jet printing process. In the ink composition of the present invention, the liquid vehicle is generally present in an amount of from about 80 to about 99.9 percent by weight, and preferably from about 90 to about 99 percent by weight.

Also contained in the ink composition of the present invention are pigment particles. The pigment can be black, cyan, magenta, yellow, red, blue, green, brown, and the like, as well as mixtures thereof. Examples of suitable pigments include various carbon blacks such as channel black, furnace black, lamp black, Raven 5250, Raven 5750, Raven 3500 and other similar carbon black products available from Columbia Company, Regal® 330, Black Pearl L, Black Pearl 1300, and other similar carbon black products available from Cabot Company, Degussa carbon blacks such as Derussol carbon black dispersions available from Degussa Company, Normandy Magenta RD-2400 (Paul Uhlich), Paliogen Violet 5100 (BASF), Paliogen Violet 5890 (BASF), Permanent Violet VT2645 (Paul Uhlich), Heliogen Green L8730 (BASF), Argyle Green XP-111-S (Paul Uhlich), Brilliant Green Toner GR 0991 (Paul Uhlich), Heliogen Blue L6900, L7020 (BASF), Heliogen Blue D6840, D7080 (BASF), Sudan Blue OS (BASF), PV Fast Blue B2G01 (American Hoechst), Irgalite Blue BCA (Ciba-Geigy), Paliogen Blue 6470 (BASF), Sudan III (Matheson, Coleman, Bell), Sudan II (Matheson, Coleman, Bell), Sudan IV (Matheson, Coleman, Bell), Sudan Orange G (Aldrich), Sudan Orange 220 (BASF), Paliogen Orange 3040 (BASF), Ortho Orange OR 2673 (Paul Uhlich), Paliogen Yellow 152, 1560 (BASF), Lithol Fast Yellow 0991K (BASF), Paliotol Yellow 1840 (BASF), Novoperm Yellow FG1 (Hoechst), Permanent Yellow YE 0305 (Paul Uhlich), Lumogen Yellow D0790 (BASF), Suco-Gelb L1250 (BASF), Suco-Yellow D1355 (BASF), Hostaperm Pink E (American Hoechst), Fanal Pink D4830 (BASF), Cinquasia Magenta (DuPont), Lithol Scarlet D3700 (BASF), Toluidine Red (Aldrich), Scarlet for Thermoplast NSD PS PA (Ugine Kuhlmann of Canada), E. D. Toluidine Red (Aldrich), Lithol Rubine Toner (Paul Uhlich), Lithol Scarlet 4440 (BASF), Bon Red C (Dominion Color Company), Royal Brilliant Red RD-8192 (Paul Uhlich), Oracet Pink RF (Ciba-Geigy), Paliogen Red 3871K (BASF), Paliogen Red 3340 (BASF), and Lithol Fast Scarlet L4300 (BASF). Other pigments can also be selected. Particularly preferred pigment particles are nonmutagenic and nontoxic carbon black particles with a polyaromatic hydrocarbon content of less than 1 ppm.

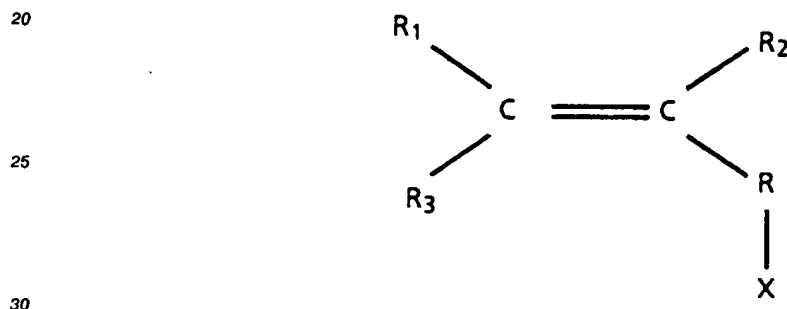
The average pigment particle diameter is from 0.001 to 10 μm ; the particle size should be as small as possible, preferably less than 3 μm and more preferably less than 1 μm , to enable a stable colloidal suspension of the particles in the liquid vehicle and to prevent unnecessary clogging of the ink channels when the ink is used in an ink jet printer having small orifice nozzles. Reduced particle size can be obtained by various processes, such as ball milling, roll milling, paintshaking, mechanical attrition, precipitation, acid pasting, and the like. Additional steps of centrifugation and filtration subsequent to treatment of the pigment particles with a vinyl aromatic salt or subsequent to mixing of the ink ingredients can assure small pigment particle size. Pigment particles to which a polymeric vinyl aromatic salt have been attached can be present in the ink composition of the present invention in any effective amount, typically from 0.1 to 15 percent by weight of the ink, and preferably from 0.5 to 8 percent by weight of the ink.

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The ink composition of the present invention also contains a polymerized vinyl aromatic salt attached to the surfaces of the pigment particles. The pigment in the ink composition of the present invention is modified and contains a polymerized vinyl aromatic salt in the form of either a homopolymer or a copolymer (when a different monomer is used together with the vinyl aromatic salt monomer) which is chemically attached to the surfaces of the pigment particles. Vinyl aromatic salts suitable for the ink composition of the present invention contain a hydrophobic moiety such as a substituted or unsubstituted aromatic group, including phenyl, naphthyl or anthracenyl, which group has a strong affinity or attraction toward the aromatic functional groups of organic pigments such as carbon blacks, phthalocyanine derivatives, anthraquinone derivatives, and other pigments containing 1 or more aromatic groups. The aromatic groups of the vinyl aromatic salt provide the needed hydrophobicity for strong adsorption onto the pigment surface. The vinyl aromatic salts also contain a hydrophilic moiety which can ionize in an aqueous liquid vehicle to form ionic charges on the pigment particles and thus result in a stable pigment dispersion. Further, the vinyl aromatic salts generally contain a polymerizable olefinic group allowing a chemical reaction or polymerization reaction to occur near the pigment particle surface to form a chemical bond between the polymerized vinyl aromatic salt and the pigment particle surface.

The pigment particles thus modified exhibit a high degree of colloidal stability in an aqueous medium through ionic charge interaction and steric hindrance.

Vinyl aromatic salts generally have the following chemical structure:



wherein R is an aromatic moiety, typically with from 6 to 20 carbon atoms, and includes phenyl, substituted phenyl, naphthyl, substituted naphthyl, anthracenyl, substituted anthracenyl, heterocyclic aromatic rings such as substituted and unsubstituted pyridinyl or quinolinyl, and X is an acid salt functional group consisting of both cation and anion moieties. Examples of cations include alkali metal ions such as Rb^+ , Cs^+ , K^+ , Na^+ , or Li^+ , organic substituted and unsubstituted ammonium ions, including ammonium, phenyl ammonium, alkyl substituted ammonium ions such as methyl ammonium, dimethyl ammonium, ethyl ammonium, diethyl ammonium, tetramethyl ammonium, tetraethyl ammonium, trimethyl ammonium and triethyl ammonium. Examples of anions include sulfonate, carboxylate, phosphate and borate; sulfonate anions are preferred. The aromatic functional group of the monomer is hydrophobic, which is desirable because it provides for affinity between the monomer and the pigment, which is important when the monomer is polymerized and chemically bonded to the pigment. The anionic moiety also enhances homogeneous distribution of the monomer in an aqueous medium to provide the grafted pigment with good colloidal stability through ionic charge repulsion. The polymerizable olefinic or vinyl group substituents R_1 , R_2 , and R_3 are independently selected from hydrogen, alkyl groups, typically with from 1 to 20 carbon atoms, aromatic groups, typically with from 6 to 20 carbon atoms, such as phenyl. Examples include vinyl (R_1 , R_2 , and R_3 are all hydrogen), methyl vinyl (for example, R_1 is $-\text{CH}_3$, R_2 and R_3 are hydrogen), ethyl vinyl (for example, R_1 is $-\text{C}_2\text{H}_5$, R_2 and R_3 are hydrogen), propyl vinyl (for example, R_1 is $-\text{C}_3\text{H}_7$, R_2 and R_3 are hydrogen), phenyl vinyl (for example, R_1 is $-\text{C}_6\text{H}_5$, R_2 and R_3 are hydrogen) and butadienyl (for example, R_1 is $-\text{C}_4\text{H}_5$, R_2 and R_3 are hydrogen). Heterocyclic groups are also suitable, such as pyridinyl (for example, R_1 is $-\text{C}_5\text{H}_4\text{N}$, R_2 and R_3 are hydrogen). The aromatic group or groups typically have from 6 to 20 carbon atoms, such as acenaphthalene (a cyclic aromatic group), methoxy phenyl, carbazyl, quinolinyl, phenothiazinyl. One example of a suitable vinyl aromatic salt is sodium para-styrene sulfonate, which is of the formula shown above wherein R is phenyl ($-\text{C}_6\text{H}_4-$), X is a sodium sulfonate salt moiety Na^+SO_3^- , and the olefinic group has three hydrogen substituents. This material is commercially available from Polyscience Inc., Warrington, Pennsylvania. Vinyl aromatic salts can also be prepared by sulfonation of the corresponding vinyl compound by any suitable method, such as by reaction with sulfonyl chloride (SO_2Cl_2), a sulfonate compound, sulfuric acid, or the like, followed by reaction with a base, such as KOH, NaOH, NH_4OH or

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LiOH, to result in the vinyl aromatic salt monomer. Reactions for the sulfonation of aromatic groups are well known, and are described in, for example, L. F. Fieser, Experiments in Organic Chemistry, (Boston, 3rd ed., 1955) page 144.

The monomeric salt can be polymerized either alone to form a homopolymer or together with another
5 monomer having a polymerizable double bond, such as olefins, substituted olefins, vinyl sulfonate, vinyl ether or styrene, to form a copolymer containing the aromatic salt. Further, the monomeric salt can be copolymerized with a vinyl aromatic sulfonic acid salt, such as sodium, potassium, lithium or ammonium, salts of moieties such as p-vinyl benzoic acid, styrene sulfonic acid, vinyl naphthalene sulfonic acid, vinyl anthracene sulfonic acid or vinyl carbazole sulfonic acid, to form a copolymer. The resulting copolymer
10 should be soluble or capable of forming a stable dispersion in the liquid vehicle selected for the ink composition.

The vinyl aromatic salt can be polymerized by placing the monomers in an aqueous system in the presence of fine pigment particles to be modified and a water soluble free radical initiator, such as sodium, potassium, or ammonium persulfate salts, diisopropylbenzene monohydroperoxide, azoisobutylamine \cdot 2HCL and its adducts, hydroperoxide (HOOH) or alkylhydroperoxide (ROOH, wherein R
15 is alkyl) in an inert environment such as vacuum, nitrogen, helium or argon, either with or without a dispersing agent such as sodium lauryl sulfate or Igepal CO-530. The polymerization reaction rate is controlled by many factors, including the reactivity of the polymerizable monomers, polymerization temperature, concentrations of impurities, chain termination substance, free radical initiator (or catalyst)
20 concentration and reaction time, Chemical modification of the pigment particles can be achieved either by first forming pigment radicals which then react with the monomeric salts through a polymerization process or by first polymerizing the monomeric salt to give a propagating polymeric radical chain which can subsequently be terminated with surface functional groups on the pigment particles. For example, the free radical initiator can polymerize the monomer, and the resulting polymeric salt is then terminated with any
25 reactive functional group of a pigment, such as phenoxy, amino, thiol or sulfide, to form a chemically modified pigment. Alternatively, the free radical initiator can react with the pigment to form a pigment radical which then either polymerizes the vinyl aromatic salt or terminates with a propagating oligomer containing the modifying monomer. When polymerization of the vinyl aromatic salt is terminated onto the pigment surface, the polymerized salt becomes chemically bonded or grafted onto the pigment particle
30 surface. When polymerization is not terminated onto the pigment surface, the polymeric salt is adsorbed onto the pigment surface as a result of the hydrophobic affinity of its aromatic moiety toward the pigment particles. The attached polymeric salt functions as a dispersing agent or a stabilizing agent for the pigment particle and enhances its colloidal stability in an aqueous medium. The modified pigment particles generally comprise pigment in an amount of from 5 to 99 percent by weight of the modified particles, and preferably
35 from 10 to 90 percent by weight of the modified particles, and the polymer in an amount of from 1 to 95 percent by weight of the modified particles, and preferably from 10 to 90 percent by weight of the modified particles. The modified particles are generally present in the ink composition of the present invention in an amount of from 0.01 to 15 percent by weight, and preferably from 1 to 10 percent by weight.

The ink composition of the present invention can also contain a dye colorant in addition to the pigment.
40 When a pigment is used as the sole colorant, the color of the formed print on a substrate is limited by the color of the pigment. When modification of the color of the images created by the pigmented ink is desired, a dye or a mixture of dyes soluble in the liquid vehicle of the ink composition can be used in conjunction with the pigment. Color balance and optimum optical density of images can be achieved by selecting an appropriate dye system and a particulate pigment system as colorants in the ink formulation. Suitable dyes
45 include Food dyes such as Food Black No. 2, Food Red No. 40, Food Blue No. 1 and Food Yellow No. 7, FD & C dyes, tetrasulfonic acid salts of phthalocyanine derivatives, including copper phthalocyanine derivatives, tetra sodium salts, tetra ammonium salts, tetra potassium salts and tetra lithium salts, Bernacid Red 2BMN; Pontamine Brilliant Bond Blue A; BASF X-34; Pontamine; Food Black 2; Carodirect Turquoise FBL Supra Conc. (Direct Blue 199), available from Carolina Color and Chemical; Special Fast Turquoise
50 8GL Liquid (Direct Blue 86), available from Mobay Chemical; Intrabond Liquid Turquoise GLL (Direct Blue 86), available from Crompton and Knowles; Cibracron Brilliant Red 38-A (Reactive Red 4), available from Aldrich Chemical; Drimarene Brilliant Red X-2B (Reactive Red 56), available from Pylam, Inc.; Levafix Brilliant Red E-4B, available from Mobay Chemical; Levafix Brilliant Red E-6BA, available from Mobay Chemical; Procion Red H8B (Reactive Red 31), available from ICI America; Pylam Certified D&C Red #28
55 (Acid Red 92), available from Pylam; Direct Brill Pink B Ground Crude, available from Crompton & Knowles; Cartasol Yellow GTF Presscake, available from Sandoz, Inc.; Tartrazine Extra Conc. (FD&C Yellow #5, Acid Yellow 23), available from Sandoz; Carodirect Yellow RL (Direct Yellow 86), available from Carolina Color and Chemical; Cartasol Yellow GTF Liquid Special 110, available from Sandoz, Inc.; D&C Yellow #10 (Acid

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Yellow 3), available from Tricon; Yellow Shade 16948, available from Tricon, Basacid Black X34, available from BASF, Carta Black 2GT, available from Sandoz, Inc.; Neozapon Red 492 (BASF); Orasol Red G (Ciba-Geigy); Direct Brilliant Pink B (Crompton-Knolls); Aizen Spilon Red C-BH (Hodagaya Chemical Company); Kayanol Red 3BL (Nippon Kayaku Company); Levanol Brilliant Red 3BW (Mobay Chemical Company);
 5 Levaderm Lemon Yellow (Mobay Chemical Company); Spirit Fast Yellow 3G; Aizen Spilon Yellow C-GNH (Hodagaya Chemical Company); Sirius Supra Yellow GD 167; Cartasol Brilliant Yellow 4GF (Sandoz); Pergasol Yellow CGP (Ciba-Geigy); Orasol Black RL (Ciba-Geigy); Orasol Black RLP (Ciba-Geigy); Savinyl Black RLS (Sandoz); Dermacarbon 2GT (Sandoz); Pyrazol Black BG (ICI); Morfast Black Conc A (Morton-Thiokol); Diazol Black RN Quad (ICI); Orasol Blue GN (Ciba-Geigy); Savinyl Blue GLS (Sandoz); Luxol Blue
 10 MBSN (Morton-Thiokol); Sevron Blue 5GMF (ICI) and Basacid Blue 750 (BASF). The dye or mixture of dyes generally is soluble in the liquid vehicle, and is present in any effective amount. Typically the dye is present in an amount of from 0 to 15 percent by weight, and preferably from 0 to 10 percent by weight.

Other additives can also be present in the ink composition of the present invention. For example, the colloidal stability of the modified pigment particles can be further enhanced by the addition of one or more
 15 dispersing agents or surfactants or wetting agents to the ink. These additives can be of the cationic, anionic, or nonionic types. Suitable surfactants, dispersing agents, and wetting agents include copolymers of naphthalene sulfonic acid salt and formaldehyde, including Daxad® 11, 11KLS, 19 and 19K, available from W.R. Grace & Company, the Lomar® D series available from Diamond Shamrock Corporation, vinyl aromatic salts available from Polyscience Company, Tamol® SN, Tamol® LG, the Triton® series available
 20 from Rohm and Haas Company, the Igepal® series available from GAF Company, the Tergitol® series, water compatible solvents such as ethylene glycol and other commercially available surfactants. These surfactants, dispersing agents, and wetting agents are generally present in amounts of from 0 to 40 percent by weight of the pigment, and preferably from 0 to 30 percent by weight of the pigment. The surfactants or dispersing agents or wetting agents coat or adsorb onto the surfaces of the pigment particles which are not
 25 occupied by the vinyl aromatic salt to create electrically charged species, and also provide steric hindrance to separate the pigment particles, thereby enabling an even more stable colloidal dispersion.

Polymeric additives can also be added to the inks of the present invention to enhance the viscosity of the ink composition and the stability of the pigment particles and to reduce the rate of agglomeration and precipitation of the particles. Water soluble polymers such as Gum Arabic, polyacrylate salts, poly-
 30 methacrylate salts, polyvinyl alcohols, polyethylene oxides, polyethylene glycols, polypropylene glycols, hydroxy propylcellulose, hydroxyethylcellulose, polyvinylpyrrolidinone, polyvinylether, starch, polyacrylamide, lignin sulfonate salts, copolymers of naphthalene sulfonate salts and formaldehyde and polysaccharides, are particularly useful for stabilizing pigment particles in a water based liquid vehicle such as water or a mixture of water and a water miscible organic liquid. Polymeric stabilizers can be present in
 35 the ink composition of the present invention in an amount of from 0 to 10 percent by weight, and preferably from 0.01 to 5 percent by weight.

Other optional additives to the ink composition of the present invention include biocides, such as Dowicil 150, 200, and 75, benzoate salts and sorbate salts, present in an amount of from 0.0001 to 4 percent by weight, and preferably from 0.01 to 2.0 percent by weight, humectants, such as ethylene glycol,
 40 diethylene glycol, propylene glycol, N-methylpyrrolidinone, hydroxyethers, ethers, amides, cyclic amides, sulfones, sulfoxides, ketones, lactones, esters and alcohols, present in an amount of from 0 to 70 percent by weight, and preferably from 3 to 40 percent by weight, antioxidants, including derivatives of phenols such as BHT and 2,6-di-t-butylphenol, tocopherol derivatives such as Vitamin E, aromatic amines, alkyl and aromatic sulfides, present in an amount of from 0 to 10 percent by weight, and preferably from 0 to 5
 45 percent by weight, pH controlling agents, including acids such as acetic acid, phosphoric acid, boric acid, sulfuric acid, nitric acid and hydrochloric acid, bases such as potassium hydroxide, sodium hydroxide, lithium hydroxide, ammonium hydroxide, trimethylamine, ethanolamine, morpholine, triethanolamine and diethanolamine, phosphate salts, carboxylate salts, sulfite salts and amine salts, present in an amount of from 0 to 10 percent by weight, and preferably from 0.001 to 5 percent by weight, drying accelerating
 50 agents, such as sodium lauryl sulfate, N,N-diethyl-m-toluamide, cyclohexylpyrrolidinone and butylcarbitol present in an amount of from 0.001 to 5 percent by weight, and preferably from 0.01 to 3 percent by weight, surface tension modifiers, such as sodium lauryl sulfate and sodium octyl sulfate, present in an amount of from 0 to 10 percent by weight, preferably from 0 to 5 percent by weight, ink penetrants, such as alcohols, sodium lauryl sulfate, esters and ketones, present in an amount of from 0.001 to 15 percent by
 55 weight, and preferably from 0.001 to 10 percent by weight, and additives for improving waterfastness and lightfastness, such as polyethyleneimine, ethylene and propylene oxide modified polyethyleneimine, present in an amount of from 0 to 10 percent by weight, and preferably from 0 to 5 percent by weight. The viscosity of the recording fluid generally is from 0.001 to 0.01 Pa.s (1 to 10 centipoises) (measured at 25 °C) and

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preferably is less than 0.003 Pa.s (3 centipoises).

The pigment modification used the present invention can be prepared by mixing the selected pigment or mixture of pigments with the selected monomeric vinyl aromatic salt of this invention in water (preferably distilled or deionized). Optionally, a wetting agent such as those of the Daxad® series of W.R. Grace (Daxad
5 ®19, 19K, 11, 11KIs), those of the Lomar® series, including Lomar® D and Lomar® W, those of the Igepal series, such as Igepal® CO 540 and Co-560, those of the Tamol® series, such as Tamol SN, those of the Triton® series, such as Triton 100, vinyl aromatic salts such as sodium para-styrene sulfonate, and organic liquids such as glycol derivatives, including ethylene glycol, diethyleneglycol, polyethylene glycol and polypropylene glycol, may be present in the mixture in an amount of from 0.1 to 50 percent by weight to
10 wet the pigment in an aqueous medium. Wetting enables the pigment to break apart to form a homogeneous aqueous dispersion ready for modification. This mixture is then attrited, for example, by placing it in a ball mill, generally at low temperatures of from 1 to 40 °C, which temperature can be maintained with external cooling, such as by surrounding with a jacket containing a circulating coolant such as water or any other suitable liquid at the appropriate temperature, which is generally cooler than room temperature and
15 warmer than 0 °C. The cooling is especially desirable when the monomeric vinyl aromatic salt is used to disperse the pigment without causing it to polymerize or be terminated prematurely. The attrition can be performed in air or under an inert atmosphere. Attrition generally continues for a period of from 0.25 to 48 hours, which results in reduction of the pigment particle size to a desirable range of from about 0.0010 to 20 µm in average particle diameter.

20 Subsequent to attrition, a water soluble free radical polymerization initiator such as potassium persulfate, hydrogen peroxide, alkyl hydroperoxides, azoisobutyronitrile derivatives, and azoisobutyrylamine·2HCl derivatives, is added to the mixture in an amount of from 0.001 to 40 percent by weight based on the amount of the vinyl aromatic salt employed. The amount of initiator added is determined according to the desired chain length of the monomer to be grafted onto the pigment, the impurities in the pigment and the
25 system. For example, larger amounts of initiator present in the system generally result in formation of lower molecular weight, relatively short chain polymers, whereas smaller amounts of initiator generally result in formation of higher molecular weight, relatively long chain polymers. Similarly, when few or no impurities are present in the mixture, generally a lesser amount of initiator is required than when impurities are present in the mixture, since the impurities may tend to terminate the chains of the polymers being formed. The
30 polymerization can be carried out under either vacuum or inert atmosphere, generally for from 0.25 to 48 hours depending on polymerization conditions, monomer reactivity, and the impurity level of the system. For example, systems containing relatively small amounts of initiator and/or relatively high amounts of impurities will require longer reaction times than systems containing larger amounts of initiator and/or few or no impurities. Depending on the reaction conditions, the degree of polymerization (i.e. the number of
35 monomer units connected together in the polymer chains) of the grafted material can vary. The polymerization process can be carried out by different methods. For example, the monomer can be mixed with the pigment together in a milling step. The free radical initiator and additional monomer, if necessary, can then be added to the milled pigment dispersion to allow polymerization to take place. Alternatively a two-stage polymerization process can be employed to modify the pigment. In this process the vinyl aromatic salt
40 monomer can be partially polymerized first with a free radical initiator, followed by addition of the pigment to be modified to the partially polymerized mixture together with additional monomer and free radical initiator, if necessary, to provide further reaction and grafting. In another variation of the two-stage polymerization process, the vinyl aromatic salt is first polymerized in the presence of a pigment with a free radical initiator, and additional needed monomer and free radical initiator are added later to the reaction
45 mixture in the second stage of polymerization. It is desirable to distribute the polymerized vinyl aromatic salt evenly throughout the surfaces of the pigment particles. A high degree of polymerization may selectively modify only a portion of the pigment particles, causing uneven distribution of the vinyl aromatic salt among the particles and possibly leading to a high viscosity for the later fabricated ink composition. A very low degree of polymerization may lead to poor pigment stability. It is believed that the optimum
50 degree of polymerization (i.e., the optimum number of monomer units in each polymer) is from 2 to 150. Typical polymerization reaction temperatures generally range from 20 °C to 120 °C, although the temperature can be outside of this range.

After the polymerization has been completed, impurities, unwanted byproducts, and excess starting materials are removed by washing the modified pigment particles with distilled or deionized water, followed
55 by centrifugation (preferably at from 1000 to 9000 R.P.M.) and removal of the supernatant liquid to isolate the modified pigment. This process is repeated as many times as necessary, usually from one to five times, to remove unwanted ionic impurities. After the purification, the modified pigment particles are mixed thoroughly (either with or without sonification) with a desired liquid vehicle which contains all the compo-

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nents of the desired ink composition, such as water, humectant, surfactant, biocide, buffering agent, anti-oxidation agent, dispersing agent and pH modifier.

The mixture may then optionally be sonified or homogenized by using an ultrasonic device such as a Bronson sonifier (sonicator) model 450 equipped with a 1.27 cm (1/2 inch) tip to assure uniform dispersion of the ingredients within the ink composition. Subsequently, the ink can be centrifuged at high speeds of from 1000 to 7000 R.P.M. for from 5 to 90 minutes to remove unstabilized pigment particles (or poorly grafted pigment particles or large pigment particles). After centrifugation, the ink is decanted and can be filtered through a filter either with or without pressure, wherein the filter has a pore size of less than 10 μm , and preferably less than 1.2 (including 0.8, 0.65, 0.45, 0.22, 0.1, 0.05 and 0.025 μm) to remove large particles and to achieve good colloidal stability.

The present invention also includes a process for generating printed images with an ink jet printer. The process comprises incorporating the ink composition disclosed herein into an ink jet printing apparatus and causing droplets of the ink to be ejected in an imagewise pattern onto a suitable substrate, thereby generating images on the substrate. Any ink jet apparatus described previously, including continuous type and drop-on-demand type, may be employed to generate images with the ink compositions of the present invention. The ink composition of the present invention may be used to form images on a wide variety of substrates, including plain papers such as Xerox® 4024 papers, including Ashdown 4024 DP, Cortland 4024 DP, Champion 4024 DP, Xerox® 4024 D.P. green, Xerox® 4024 D.P. pink and Xerox® 4024 D.P. yellow, Xerox® 4200 papers, Xerox® 10 series paper, canary ruled paper, ruled notebook paper, bond paper such as Gilbert 25 percent cotton bond paper, Gilbert 100 percent cotton bond paper, and Strathmore bond paper, silica coated papers such as Sharp Company silica coated paper and JuJo paper, transparency materials such as Xerox® 3R3351, Tetrionix ink jet transparencies and Arkright ink jet transparencies, fabrics, textile products, plastics, polymeric films, inorganic substrates such as metals and wood.

Ink compositions of the present invention exhibit significant advantages, particularly when employed in ink jet printing processes. For example, images generated with the inks of the present invention typically exhibit high lightfastness, generally in excess of 95 percent, exhibit high waterfastness, generally in excess of 95 percent, exhibit high optical density, generally from 1.0 to 1.45 optical density units on plain paper substrates and from 1.2 to 1.78 optical density units on silica coated papers, and exhibit high resolution, with resolutions of 300 spots per 2.54 cm (inch) and greater being easily obtained. The advantages of high waterfastness, high lightfastness, and high resolution are all obtainable on plain paper substrates.

Specific embodiments of the invention will now be described in detail. All parts and percentages are by weight unless otherwise indicated.

EXAMPLE I**IA. Preparation of Pigment Dispersion Prior To Polymerization:**

Carbon black (Raven® 5250 bead form, obtained from Columbia Chemical Company, 60 g), sodium para-styrene sulfonate salt (monomer, also functioning as a wetting agent for carbon black, obtained from Polyscience Company, 12 g), and distilled water (228 g) were added portionwise to an attritor (Union Process Company Model OV-1 equipped with a cooling jacket to remove heat) containing 1500 g of 0.32 cm (1/8 inch) in diameter stainless steel shot while milling. The attritor was operated at 53 to 55 V. After milling for about 8 h, the pigment dispersion was removed from the attritor with portionwise water dilution (total 120 g of distilled water added to remove the dispersion, resulting in recovery of 400 g (95% recovery yield) of the carbon black pigment dispersion in water containing the monomeric sodium parastylene sulfonate salt.

IB. Polymerization Process and Treatment of Pigment Dispersion:

To a three-necked flask equipped with a magnetic stirrer, a thermometer, a gas bubbler, a dropping funnel, and connections to vacuum and inert gas lines were added 112 g of the carbon black pigment dispersion prepared in IA (containing 16 g of carbon black and 3.2 g of monomer) and a vinyl aromatic salt monomer (sodium para-styrene sulfonate) solution (1.6 g of monomer in 10 g of distilled water). A free radical initiator solution of potassium persulfate (1.57 g in 40 ml of distilled water) was introduced through the dropping funnel. The flask was then evacuated and purged with argon several times to remove air and was finally filled with argon. The mixture was allowed to polymerize in an oil bath at 70 °C (controlled by a temperature control unit) overnight (about 16 h) followed by heating the mixture to reflux for 2 h. The resulting dispersion of carbon black having grafted thereto the polymerized sodium para-styrene sulfonate

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was then allowed to cool to room temperature under an inert atmosphere. Subsequently, the pH of the pigment dispersion was adjusted from 1.86 to 7.2 by the addition of 0.5 m potassium hydroxide solution. The dispersion was then centrifuged at 5500 R.P.M. for 30 min and the supernatant containing unreacted monomer byproducts and undesired water soluble materials was removed from the solid pigment.

5 Thereafter, the pigment was redispersed in distilled water and centrifuged at 5500 R.P.M. for 1 h, after which the supernatant containing unwanted electrolytes, unwanted monomer and impurities was removed from the pigment by decantation. Subsequently, 16 g of the purified modified carbon black was then added to 152 g of distilled water to result in a dispersion (168 g) of the modified pigment.

10 **IC. Ink Preparation:**

To 84 g of the modified pigment dispersion prepared in IB was added with stirring ethylene glycol (40 g) biocide (Dowicil 200, 0.08 g), 3.2 g of a 20 percent by weight of sodium lauryl sulfate solution in water (prepared with Duponol Me Dry obtained from DuPont Company; 3.2 g of solution contained 0.64 g of the solid sodium lauryl sulfate), and distilled water (37.7 g). The resulting ink mixture was agitated and homogenized with a Bronson sonicator (also known as a sonifier) equipped with a 0.01 mm (1/2") tip for 10 min. Subsequently, the liquid mixture was centrifuged for 30 min at 5500 R.P.M. and the suspended ink was decanted and filtered easily through 5 μ m and 3 μ m filters. The ink composition exhibited a viscosity of 0.00419 Pa.s (4.19 centipoises (c.p)) measured at 25 ° C.

20

ID. Generation of Prints:

The ink composition prepared in IC was incorporated into an ink cartridge in a thermal ink jet printing test fixture equipped with a 48 jet printhead (about 300 spots per 2.54 cm (inch) resolution). The voltage applied to the heater was in the range of 30 to 42 V, with a pulse length of 2 to 3 μ s. the printhead was maintained at a temperature from 10 to 60 °C during the imaging process. Very Good images were obtained on plain papers including Xerox 10 series paper and Xerox letterhead paper with this thermal ink jet printing device. Specifically, the images exhibited excellent waterfastness after they were dried, exhibited excellent lightfastness comparable to that obtained with images generated by xerographic processes, exhibited high optical densities, and had sharp images with little or no feathering. In addition, the ink was jetted from the test fixture to generate images even after the fixture containing the ink had been allowed to remain idle for 100 at 15 percent relative humidity.

EXAMPLE II

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An ink composition was prepared by mixing together 84 g of a dispersion of modified pigment particles prepared as described in IB above, biocide (Dowicil 200 0.08 g), propylene glycol (40 g), distilled water (32.7 g) and 3.0 g of a solution of sodium lauryl sulfate in water (containing 20 percent by weight of sodium lauryl sulfate). The resulting ink mixture was sonicated for 10 min and centrifuged at 5500 R.P.M. for 30 min. Subsequently, the ink was decanted and filtered easily through 5 μ m and 3 μ m membrane filters. Thereafter, a dispersing agent (Daxad 19 K. 30 g of a 20 percent solution in water containing a total of 0.6 g of the solid dispersing agent) was added to the ink mixture and the ink was sonicated for 10 min, resulting in an ink containing about 3.7 percent by weight of carbon black pigment particles having attached thereto a polymerized vinyl aromatic salt.

45

EXAMPLE III

An ink composition was prepared by mixing together 40 g of an ink prepared as described in IC above and a dispersing agent (Daxad 19 K, a copolymer of sodium naphthalene sulfonate and formaldehyde, 0.084 g of dispersing agent in 0.75 g of water). The resulting ink was sonicated for 10 min cooled, and filtered through a 3 μ m membrane filter, resulting in an ink with a viscosity of 0.00199 Pa.s (1.99 c.p.)

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EXAMPLE IV**IVA. Pigment Modification (In situ polymerization of vinyl aromatic salt in the presence of pigment):**

5 To a 500 ml three-necked flask equipped with a stirrer, a thermometer, a gas bubbler, and connections to vacuum and argon lines was added 105 g of a pigment dispersion prepared according to the method of Example IA above, sodium para-styrene sulfonate salt (1.5 g in 10 ml of water), and potassium persulfate (free radical initiator, 1.18 g in 20 ml of distilled water). The pigment mixture containing the monomer
10 initiator was degassed several times by vacuum evacuation and refilling with argon. Subsequently, the pigment mixture was slowly heated to 70 °C and held at that temperature overnight (15 h) and was then heated to reflux temperature for 1 h. Thereafter, the mixture was cooled in an inert atmosphere and the mixture was adjusted from pH = 2.04 to pH = 7.3 by the addition of a potassium hydroxide (0.5 m) solution. The mixture was then centrifuged and the modified pigment (50.3 g) was isolated from the
15 aqueous liquid which contained byproducts, unpolymerized monomer, and unused initiator. Subsequently, the modified pigment was dispersed in 300 g of distilled water, centrifuged, and isolated to result in purified modified pigment particles, which were thereafter redispersed in distilled water to form 217.8 g of a pigment dispersion suitable for ink preparation.

IVB. Ink Preparation:

20 To 108.9 g of the chemically modified pigment dispersion prepared in IVA above was added ethylene glycol (37.5 g), Dowicil 200 (0.075 g), and 3.75 g of a 20 percent solution of sodium lauryl sulfate (Duponol Me Dry) in water. The resulting ink was sonicated for 10 min and then centrifuged at 5500 R.P.M. for 30
25 min. The suspended liquid pigment mixture was then decanted and filtered through a 1.2 µm filter to result in an ink containing about 4.5 percent by weight of carbon black pigment particles having attached thereto a polymerized vinyl aromatic salt. The viscosity of this ink measured at 25 °C was 0.0027 Pa.s (2.17 c.p.).

IVC. Preparation of an Additional Ink:

30 A copolymer of potassium naphthalene sulfonate and formaldehyde (Daxad 19 K, 0.171 g) was added with stirring to 20 g of the ink prepared in IVB above. The resulting ink was filtered easily through a 0.65 µm membrane filter to result in an ink composition.

EXAMPLE V

35 A nonionic surfactant (or dispersing agent), Igepal CO-630 (0.09 g, obtained from GAF Corporation) was added to 20 g of an ink prepared as described in Example IVB above to result in an ink with a viscosity of 0.00318 Pa.s (3.18 c.p.) at 25 °C.

EXAMPLE VI**Ink Preparation Via a Two Stage Polymerization Process For Pigment Modification****VIA. Preparation of Pigment Dispersion:**

45 A carbon black pigment dispersion was prepared by milling Raven® 5250 bead form (60 g, obtained from Columbia Chemical Company), sodium para-styrene sulfonate salt (a monomer which was also used as a wetting agent in dispersing the pigment, 12 g), and distilled water (283 g) in an attritor (Union Process Company modified Model OV-1) equipped with a water cooling jacket and 1500 g of 0.32 cm (1/8 inch) in
50 diameter stainless steel shot for 8 h. After milling, the pigment dispersion was removed from the attritor and diluted by the addition of 85 ml of distilled water. A pigment dispersion (406.5 g) containing 13.6 percent by weight carbon black was obtained, wherein the carbon black particles contained 27 percent by weight of vinyl aromatic salt monomer.

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EP 0 475 075 B1**VIB. Modification of Pigment Particles by a Two Stage Polymerization of a Vinyl Aromatic Salt Monomer:**

To a three-necked flask equipped with a stirrer, a dropping funnel, a thermometer, a gas bubbler, and vacuum and argon lines was added sodium para-styrene sulfonate salt (3.0 g), distilled water (30 ml), and potassium persulfate ($K_2S_2O_8$, free radical initiator, 0.787 g).

The initiator to monomer ratio was 26.2 percent by weight (first stage of polymerization mixture). The mixture was stirred thoroughly to form a homogeneous solution. Pigment dispersion prepared as described in Example VIA (115.5 g) and potassium persulfate initiator solution (0.826 g initiator in 30 g distilled water) were placed in the dropping funnel. The entire system was evacuated, degassed, and purged several times with argon, and the monomer mixture in the three-necked flask was heated to 70 °C and held at that temperature for 90 min to polymerize part of the monomer (first stage of polymerization) to an oligomeric polystyrene sulfonate salt. Subsequently, the pigment dispersion containing the monomer and free radical initiator in the dropping funnel was added to the three-necked flask. The entire mixture was then heated to 70 °C for overnight (about 15 h) and thereafter refluxed for 1 h. After cooling to room temperature under an inert atmosphere, the modified carbon black pigment dispersion was adjusted from pH = 2.55 to 7.5 by the addition of a 0.5 m potassium hydroxide solution (12.14 g). The entire liquid mixture was centrifuged at 5500 R.P.M. for 30 min, after which the suspended liquid was removed and the settled pigment solid was washed and redispersed with 300 ml of distilled water. The resulting liquid mixture was washed and redispersed with a sonicator (10 min) to form a homogeneous carbon black dispersion. This dispersion contained about 47.4 percent by weight of the monomer used in the modification of carbon black pigment particles, indicating that about 47.4 percent by weight of the monomer initially added to the system ultimately became attached to the pigment.

VIC. Ink Preparation:

A solution of ethylene glycol (humectant, 37.5 g), Dowicil 200 (0.075 g), and Duponol Me Dry (sodium lauryl sulfate, 3.75 g of a 20 percent solution in water) was slowly added to 77.5 g of the modified pigment dispersion of VIB above with stirring. The resulting ink mixture was sonicated for 10 min and centrifuged at 5500 R.P.M. for 30 min after which the suspended liquid containing modified pigment particles was filtered through a 3 μ m filter to result in an ink with a viscosity of 0.0028 Pa.s (2.8 c.p.).

EXAMPLE VII

An ink containing 4.67 percent by weight of carbon black particles having attached thereto a polymerized vinyl aromatic salt, 25 percent by weight of ethylene Glycol, 0.5 percent of sodium lauryl sulfate, and 0.05 percent by weight of Dowicil 200 was prepared by the method of Example VIC except the ink's modified pigment particles were prepared with a monomer to initiator ratio of 13.0 percent by weight instead of 26.2 percent by weight as indicated in the first stage of polymerization in Example VIB. The ink exhibited a viscosity of 0.00275 Pa.s (2.75 c.p.) at 25 °C and the viscosity of this recording remained stable after at least 2 months storage.

EXAMPLE VIII**VIIIA. Attrition of Carbon Black Pigment with a Wetting Medium of an Organic Solvent:**

To a jacketed attritor (modified Union Processes Company Model OV-1) was added slowly with stirring 1500 g of 0.32 cm (1/8 inch) in diameter stainless steel shot, distilled water (125 g), ethylene glycol (120 g), and carbon black pigment (Raven 5250, 60 g). The mixture was milled for 8 h at a setting of 70 V. Additional water (195 g) was then added to the attritor and the mixture was milled for 1 h to form a homogeneous mixture. About 457.5 g of the pigment dispersion was subsequently removed from the attritor (91.5 percent yield).

VIIIB. Pigment Modification Using a Two Stage Polymerization Process:

To a three-necked flask equipped with a thermometer, a stirrer, a dropping funnel, a gas bubbler, and connections to vacuum and argon lines was added sodium para-styrene sulfonate salt (7.5 g), potassium persulfate ($K_2S_2O_8$ initiator, 1.49 g), and distilled water (150 g). Pigment dispersion prepared as in VIIIA

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above (125 g, containing 15 grams of carbon black) and distilled water (30 g) were placed in the dropping funnel which was attached to the three-necked flask. The monomer mixture in the flask was stirred and degassed several times with vacuum evacuation and purging with argon and was then heated to 70 °C with stirring and held at that temperature for 4 h before the addition of the carbon black dispersion mixture from the dropping funnel. After the addition of the carbon black dispersion into the flask, the mixture was heated at 70 °C for 15 h and then at reflux temperature (about 103 °C) for 1 h. After cooling in the inert atmosphere, the pH of the modified pigment mixture was adjusted from 4.0 to 7.3 by the addition of a 0.5 m potassium hydroxide solution (9.17 g). Subsequently, the pigment mixture was centrifuged and decanted to remove the aqueous liquid layer from the solid. The solid pigment was then diluted with distilled water (300 g) with stirring and centrifuged at 5500 R.P.M. for 30 min, followed by separating the liquid from the modified pigment solid to remove undesired water soluble impurities. The modified pigment was thereafter redispersed in distilled water to form a pigment dispersion (201.3 g) which was ready for later preparation of ink. Based on the data of solid content in the removed aqueous liquid layer it was estimated that 21.7 percent of the monomer was grafted and/or adsorbed onto the carbon black pigment.

VIIIC. Ink Preparation:

A solution was prepared by mixing together ethylene glycol (37.5 g), Dowicil 200 (0.075 g), and a 20 percent solution of sodium lauryl sulfate in water (3.75 g), and the solution was added slowly with stirring to 100.6 g of the modified carbon black pigment dispersion prepared in VIIIB above. The resulting ink mixture was sonicated for 10 minutes and then centrifuged at 5500 R.P.M. for 30 min. The suspended pigmented ink was filtered through 5.0 µm and 1.2 µm filters, resulting in an ink with a viscosity of 0.0028 Pa.s (2.8 c.p.) as measured at 25 °C. The viscosity of the ink was stable for at least 6 months.

VIIID. Preparation of an Ink Containing Modified Pigment Particles and a Dye:

Food Black No. 2 Dye (obtained from Mobay Chemical Company, 1.0 g was added to 50 g of the ink prepared in VIIIC above and the resulting ink was filtered through a membrane filter (0.65 µm pore size) to give an ink containing a dye.

VIIIE. Additional Ink Modification:

A cyan dye (copper phthalocyanine-3,4',4'',4'''- tetrasulfonic acid tetrasodium salt (obtained from Aldrich Chemical Company, 0.15 g was added to 30 g of the ink prepared in VIIID, and the resulting ink was filtered easily through a 0.65 µm filter.

EXAMPLE IX**Ink Preparation Process Employing Two Stage Polymerization Process for Modification of Pigment Particles**

To a three-necked flask equipped with a thermometer, a dropping funnel, a stirrer, a gas bubbler, and connections to vacuum and argon lines was added with stirring 125 g of a carbon black pigment dispersion prepared as described in Example VIIIA above, a solution of sodium para-styrene sulfonate salt (3.75 g of monomer), and potassium persulfate ($K_2S_2O_8$, 0.99 g in 25 g of distilled water). A similar aqueous solution containing sodium para-styrene sulfonate (3.75 g) and potassium persulfate (free radical initiator, 0.99 g) in distilled water (25 g) was placed in the dropping funnel. After degassing and purging the system with vacuum and argon, the pigment mixture was heated to 80 °C for 4 h, after which the monomer mixture in the dropping funnel was slowly added to the flask. The entire mixture was subsequently heated at 80 °C for overnight (about 15 h). The pigment mixture was thereafter heated to reflux temperature for 1 h. After adjusting the pH from 2.93 to 7.3 by the addition of a 0.5 m potassium hydroxide solution, the pigment mixture was centrifuged at 6000 R.P.M. for 40 min and the liquid layer was poured off from the solid. The modified solid pigment was then dispersed in distilled water to form a pigment dispersion (162.8 g) which was suitable for the subsequent preparation of ink.

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IXB. Ink Preparation:

A solution containing ethylene glycol (37.5 g), sodium lauryl sulfate (3.75 g of a 20 percent sodium lauryl sulfate solution in water) and Dowicil 200 (0.075 g) was slowly added with stirring to 81.4 g of the pigment dispersion of IXB above. The mixture was then sonicated for 10 min and centrifuged at 5500 R.P.M. for 30 min. After the centrifugation, the suspended ink mixture was filtered through 5 μm and 1.2 μm filters to result in an ink.

EXAMPLE X

Chemically modified pigment dispersions were characterized to determine the percentage of the monomer polymerized (based on the weight of monomer used) and attached to the pigment as well as the weight percentage of monomer (vinyl aromatic salt, sodium para-styrene sulfonate) being polymerized or grafted onto the pigment based on the weight of carbon black pigment used. These values were determined by measuring the initial weight of unmodified pigment particles added, the weight of vinyl aromatic salt monomers initially added, and the weight of modified pigment particles formed. By subtracting the weight of unmodified pigment from the weight of modified pigment, the amount of monomer that polymerized and became attached to the pigment was determined. The weight percent of monomer polymerized and attached to the pigment was determined by dividing the weight of monomer that became attached to the pigment by the weight of monomer initially added to the system and multiplying by 100. The weight percent of monomer attached to the pigment represents the relative amounts of pigment and polymer in each particle; for example, 1.144 g of the pigment dispersion of Example IC as shown in the first row of the table contains 1 gram of carbon black and 0.144 g of polymerized vinyl aromatic salt. Table 1 contains this data for inks and dispersions prepared according to the indicated Examples herein.

TABLE 1

Pigment Dispersion or Ink (Example No.)	Weight % monomer polymerized and attached to pigment (efficiency of monomer polymerized)	Weight % monomer attached to pigment (based on weight of pigment)
IC	48	14.4
IVB	44.6	13.4
V	44.6	13.4
VII	35.3	14.1
IXB	35.2	17.6

EXAMPLE XI

A thermal ink jet test fixture equipped with a 48 jet printhead with a resolution of 288 spi was employed for printing with inks of the present invention. The printhead was operated at 33.5 V with a pulse length of 3 μs . Images with several inks of the present invention were prepared on different plain papers and silica coated paper. Excellent sharp characters and graphics were obtained without feathering. Images prepared by the inks of the present invention were extremely waterfast and lightfast. Images were not destroyed if water was spilled on the imaged papers. Extremely dark images with high optical density were obtained. Some of the optical density data after the background correction are listed below in Table 2 for inks prepared according to the indicated Example herein. Dashed lines in the table represent papers for which no tests were done with the indicated ink. The papers listed are as follows:

Paper A Gilbert Bond
 Paper B Strathmore Bond
 Paper C Xerox 4024 DP Ashdown
 Paper D Xerox 4200 DP Ashdown
 Paper E Xerox 10 Series DP
 Paper F Xerox 10 Series Smooth
 Paper G Xerox Letterhead

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Paper H Silica coated (Sharp Company)

TABLE 2

5	Ink (Example No.)	Paper A	Paper B	Paper C	Paper D	Paper E	Paper F	Paper G	Paper H
	IIC	1.46	1.41	1.47	1.45	1.42	1.43	1.43	1.68
	III	1.23	1.30	1.25	1.27	1.19	1.23	1.32	1.52
10	IVB	1.38	1.41	1.37	1.37	1.40	1.41	1.46	1.58
	V	1.42	1.43	1.44	1.46	1.39	1.37	1.36	1.54
	VII	1.42	1.40	1.40	1.32	1.26	---	1.33	---
15	VIIID	1.39	1.33	1.41	1.30	1.25	---	1.34	1.72
	IXB	1.31	1.34	1.34	1.35	1.30	---	1.31	1.68

EXAMPLE XII

Solid area and line images prepared on paper substrates with the inks of this invention exhibited electrical conductivity. A solid line image was generated with the test fixture described in Example XI on flexible paper substrates, with the solid image having dimensions of 1.65 cm (width) x 12.9 cm (length) except as otherwise specified. Resistance was measured across the line with an Ohm meter and indicated as kilo ohm per centimeter, and the sheet resistivity was calculated in terms of kilo ohm per square centimeter area. Conductivity data for images on the papers indicated with inks prepared according to the indicated Example herein are contained in Table 3. The papers indicated are as in Example XI.

TABLE 3

30	Ink (Example No.)	Paper A		Paper C		Paper F		Paper H	
35		measured (K Ω /cm)	sheet (K Ω /cm ²)	measured (K Ω /cm)	sheet (K Ω /cm ²)	measured (K Ω /cm)	sheet (K Ω /cm ²)	measured (K Ω /cm)	sheet (K Ω /cm ²)
	IC	9.3	15.3	14.7	24.3	15.5	25.6	60	99
	VII	8.8	14.6	10.1	16.6	19.8	32.6	20.9	24.5
	VIIID	10.6	4.24†	10.1	16.6	27.9	46	26.7	21.4*
40	IXB	6.3	10.4	9.9	29.2	17.1	28.1	31.0	24.8*

†: solid area dimensions - 0.4 cm (width) x 12.9 cm (length)

*: solid area dimensions - 0.8 cm (width) x 12.9 cm (length)

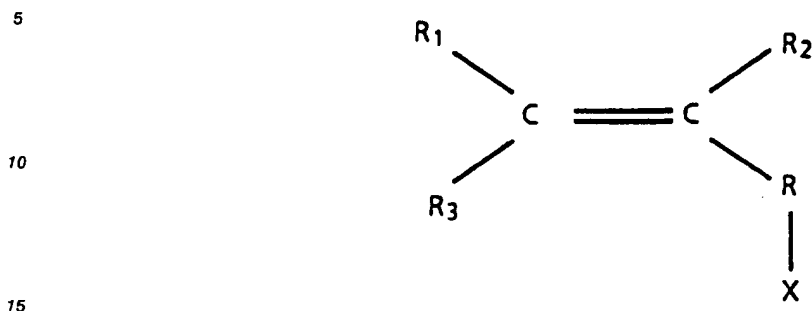
Claims

1. An ink composition comprising an aqueous liquid vehicle and pigment particles having chemically grafted to the surfaces thereof a polymerized vinyl aromatic salt in the form of a homopolymer or a copolymer.
2. The ink composition of claim 1 wherein the pigment is carbon black.
3. The ink composition of claim 1 wherein the pigment particles are nonmutagenic nontoxic carbon black particles with a polyaromatic hydrocarbon content of less than 1 ppm.
4. The ink composition of claim 1 wherein the pigment is selected from the group consisting of cyan pigment, magenta pigments, yellow pigments, red pigments, blue pigments, green pigments, orange

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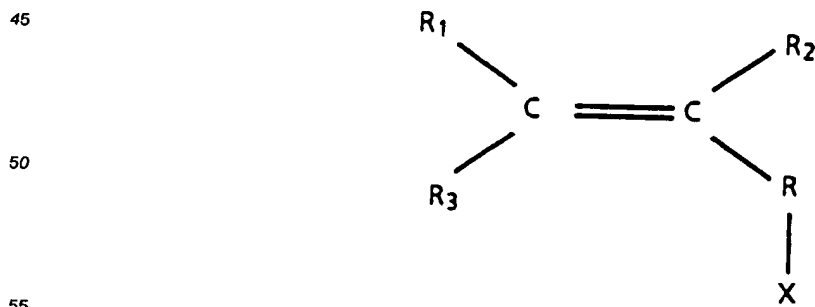
pigments, and mixtures thereof.

5. The ink composition of claim 1 wherein the vinyl aromatic salt is of the formula



wherein R is an aromatic moiety, X is an acid salt functional group, and R₁, R₂, and R₃ are independently selected from the group consisting of hydrogen, alkyl groups, substituted alkyl groups, aromatic groups, substituted aromatic groups, heterocyclic groups, and substituted heterocyclic groups.

6. The ink composition of claim 1 wherein the liquid vehicle comprises water and a humectant.
7. The ink composition of claim 6 wherein the humectant is selected from the group consisting of ethylene glycol, propylene glycol, diethylene glycols, glycerine, dipropylene glycols, polyethylene glycols, polypropylene glycols, amides, ethers, carboxylic acids, esters, alcohols, organosulfides, organosulfoxides, sulfones, alcohol derivatives, carbitol, butyl carbitol, cellusolve, ether derivatives, amino alcohols, ketones, and mixtures thereof.
8. The ink composition of claim 6 wherein the liquid vehicle comprises water in an amount of from 40 to 100 percent by weight and a humectant in an amount of from 0 to 60 percent by weight.
9. The ink composition of claim 1 wherein the pigment particles have an average particle diameter of from 0.001 to 10 μm .
10. The ink composition of claim 1 wherein the pigment particles have an average particle diameter of less than 1 μm .
11. The ink composition of claim 1 wherein the pigment particles having the polymerized vinyl aromatic salt chemically grafted to the surfaces thereof are present in the ink composition in an amount of from 0.1 to 15 percent by weight.
12. The ink composition of claim 1 wherein the vinyl aromatic salt is of the formula

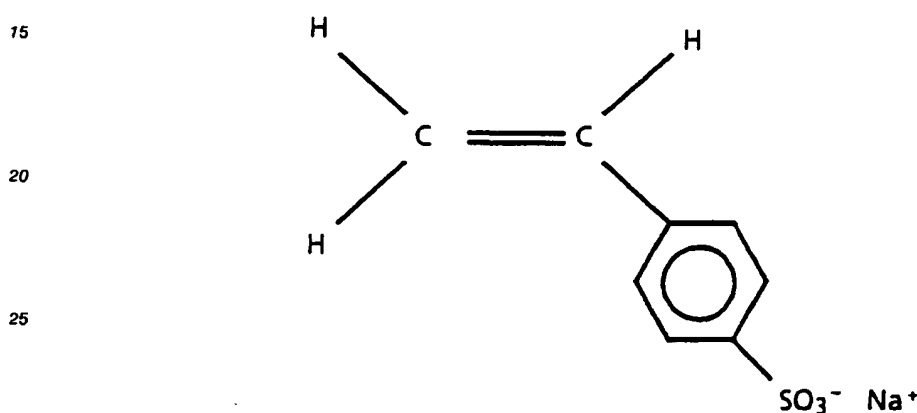


wherein R is an aromatic moiety with from 6 to 20 carbon atoms, X is an acid salt functional group consisting of both cation and anion moieties, and R₁, R₂, and R₃ are independently selected from the

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group consisting of hydrogen, alkyl groups with from 1 to 20 carbon atoms, aromatic groups with from 6 to 20 carbon atoms, and heterocyclic groups.

13. The ink composition of claim 12 wherein R is selected from the group consisting of phenyl, substituted phenyl, naphthyl, substituted naphthyl, anthracenyl, substituted anthracenyl, and heterocyclic aromatic rings.
14. The ink composition of claim 12 wherein X is a salt functional group wherein the cation is selected from the group consisting of Rb^+ , Cs^+ , K^+ , Na^+ , Li^+ , ammonium, and substituted ammonium, and the anion is selected from the group consisting of sulfonate, carboxylate, phosphate, and borate.
15. The ink composition of claim 1 wherein the vinyl aromatic salt is of the formula

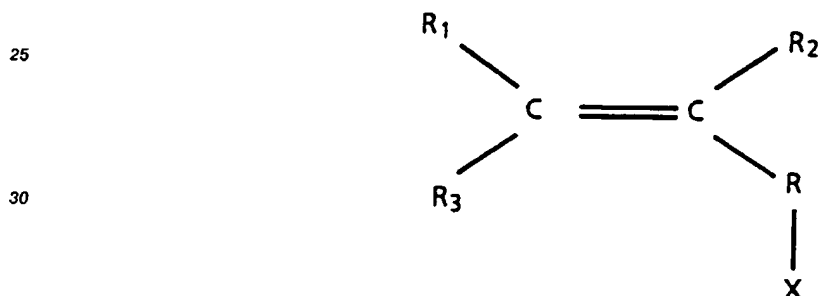


16. The ink composition of claim 1 wherein the vinyl aromatic salt is a styrene sulfonate salt.
17. The ink composition of claim 1 which also contains a dye.
18. The ink composition of claim 17 wherein the dye is present in an amount of no more than 15 percent by weight.
19. The ink composition of claim 1 which also contains a dispersing agent selected from the group consisting of cationic dispersing agents, anionic dispersing agents, and nonionic dispersing agents.
20. The ink composition of claim 19 wherein the dispersing agent is present in an amount of no more than 40 percent by weight.
21. The ink composition of claim 1 which also contains a water soluble polymeric additive.
22. The ink composition of claim 21 wherein the polymeric additive is selected from the group consisting of Gum Arabic, polyacrylate salts, polymethacrylate salts, polyvinyl alcohols, polyethylene oxides, polyethylene glycols, polypropylene glycols, hydroxy propylcellulose, hydroxyethylcellulose, polyvinylpyrrolidinone, polyvinylether, starch, polyacrylamide, lignin sulfonate salts, copolymers of naphthalene sulfonate salts and formaldehyde, and polysaccharides.
23. The ink composition of claim 21 wherein the polymeric additive is present in an amount of from 0.01 to 5 percent by weight.
24. A process for preparing an ink composition which comprises mixing in water a pigment and a vinyl aromatic salt, attriting the mixture until the pigment particles have an average particle diameter of from 0.001 to 20 μm , adding to the mixture a water soluble free radical polymerization initiator and heating

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the mixture under vacuum or inert atmosphere, thereby polymerizing the vinyl aromatic salt and chemically grafting it to the pigment particle surfaces, separating the pigment particles from the mixture, and admixing the pigment particles with a liquid vehicle.

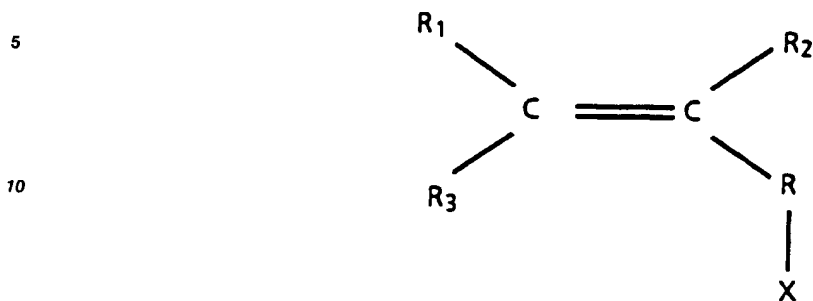
- 5 25. The process of claim 24 wherein subsequent to admixing the pigment particles with the liquid vehicle, the ink composition is subjected to centrifugation and filtration to remove pigment particles with an average particle diameter of greater than 1 μm .
- 10 26. The process of claim 24 wherein polymerization of the monomeric vinyl aromatic salt is carried out at a temperature of from 20 to 120 °C.
27. The process of claim 24 wherein the mixture of water, pigment, and monomeric vinyl aromatic salt is attrited for a period of from 0.25 to 48 hours.
- 15 28. The process of claim 24 wherein prior to polymerization the mixture comprises water in an amount of from 35 to 98 percent by weight, pigment particles in an amount of from 2 to 65 percent by weight, monomeric vinyl aromatic salt in an amount of from 0.02 to 50 percent by weight, a free radical polymerization initiator in an amount of from 0.01 to 15 percent by weight, and a wetting agent in an amount of from 0 to 50 percent by weight.
- 20 29. The process of claim 24 wherein the vinyl aromatic salt is of the formula



- wherein R is an aromatic moiety, X is an acid salt functional group, and R₁, R₂, and R₃ are independently selected from the group consisting of hydrogen, alkyl groups, substituted alkyl groups, aromatic groups, substituted aromatic groups, heterocyclic groups, and substituted heterocyclic groups.
- 40 30. The process of claim 29, wherein R is selected from the group consisting of phenyl, substituted phenyl, naphthyl, substituted naphthyl, anthracenyl, substituted anthracenyl, and heterocyclic aromatic rings.
31. The process of claim 24 wherein the pigment particles having chemically grafted to the surfaces thereof the polymerized vinyl aromatic salts have an average particle diameter of from 0.001 to 10 μm .
- 45 32. The process of claim 24 wherein the pigment particles having chemically grafted to the surfaces thereof the polymerized vinyl aromatic salts have an average particle diameter of less than 1 μm .
- 50 33. The process of claim 24 wherein the pigment particles having the polymerized vinyl aromatic salt chemically grafted thereto are present in the ink composition in an amount of from 0.1 to 15 percent by weight.

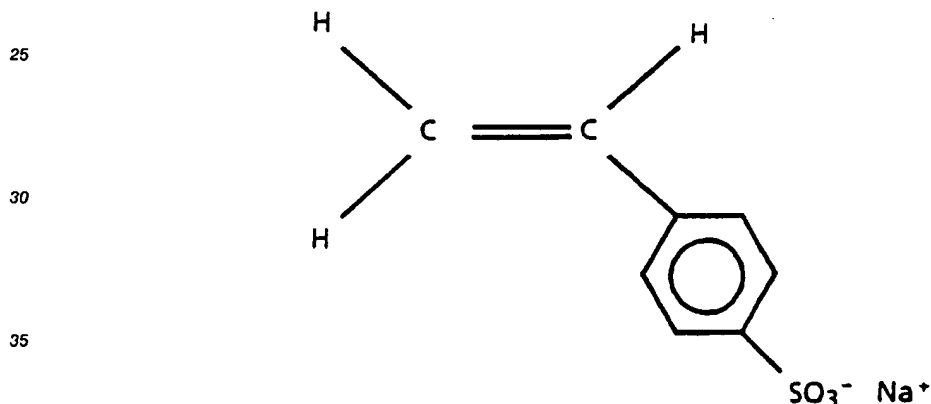
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34. The process of claim 24 wherein the vinyl aromatic salt is of the formula



wherein R is an aromatic moiety with from 6 to 20 carbon atoms, X is an acid salt functional group consisting of both cation and anion moieties, and R₁, R₂ and R₃ are independently selected from the group consisting of hydrogen, alkyl groups with from 1 to 20 carbon atoms, aromatic groups with from 6 to 20 carbon atoms, and heterocyclic groups.

35. The process of claim 24 wherein the vinyl aromatic salt is of the formula



36. The process of claim 24 wherein the vinyl aromatic salt is a styrene sulfonate salt.

37. A process for preparing an ink composition which comprises:

a. preparing modified pigment particles by:

45 i. first mixing together in water a free radical polymerization initiator and a monomeric vinyl aromatic salt and heating the mixture under vacuum or inert atmosphere, thereby polymerizing the vinyl aromatic salt; and

50 ii. subsequently adding to the polymerized vinyl aromatic salt pigment particles with an average particle diameter of from 0.001 to 10 μm, additional vinyl aromatic salt monomers, and, optionally free radical polymerization initiator, thereby further polymerizing the vinyl aromatic salt and resulting in chemical grafting of the polymerized vinyl aromatic salt to the surfaces of the pigment particles; and

b. admixing the modified pigment particles thus prepared with a liquid vehicle.

55 38. A process for preparing an ink composition which comprises:

a. preparing modified pigment particles by:

i. first mixing together in water pigment particles with an average particle diameter of from 0.001 to 10 μm, a monomeric vinyl aromatic salt, and a free radical polymerization initiator and heating

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the mixture under vacuum or inert atmosphere, thereby polymerizing the vinyl aromatic salts; and
 ii. subsequently adding to the mixture additional vinyl aromatic salt monomers and, optionally,
 additional free radical polymerization initiator, thereby further polymerizing the vinyl aromatic salt,
 wherein the polymerized vinyl aromatic salt is chemically grafted to the surfaces of the pigment
 particles; and

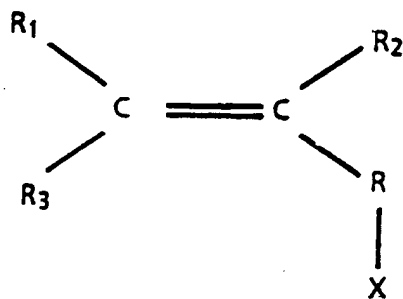
b. admixing the modified pigment particles thus prepared with a liquid vehicle.

39. A process for generating images onto a substrate which comprises incorporating into an ink jet printing
 apparatus an ink composition comprising an aqueous liquid vehicle and pigment particles having
 chemically grafted to the surfaces thereof a polymerized vinyl aromatic salt in form of a homopolymer
 or a copolymer and causing droplets of the ink composition to be ejected in an imagewise pattern onto
 the substrate.

40. The process of claim 39 wherein the substrate is selected from the group consisting of plain paper,
 silica coated paper, transparency material, fabric, and plastic.

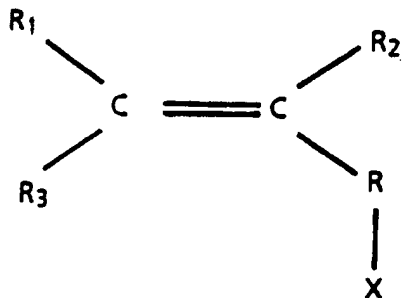
41. The process of claim 39 wherein the ink jet printing apparatus is a thermal ink jet printer.

42. The process of claim 39 wherein the vinyl aromatic salt has monomers of the formula



wherein R is an aromatic moiety, X is an acid salt functional group, and R₁, R₂, and R₃ are
 independently selected from the group consisting of hydrogen, alkyl groups, substituted alkyl groups,
 aromatic groups, substituted aromatic groups, heterocyclic groups, and substituted heterocyclic groups.

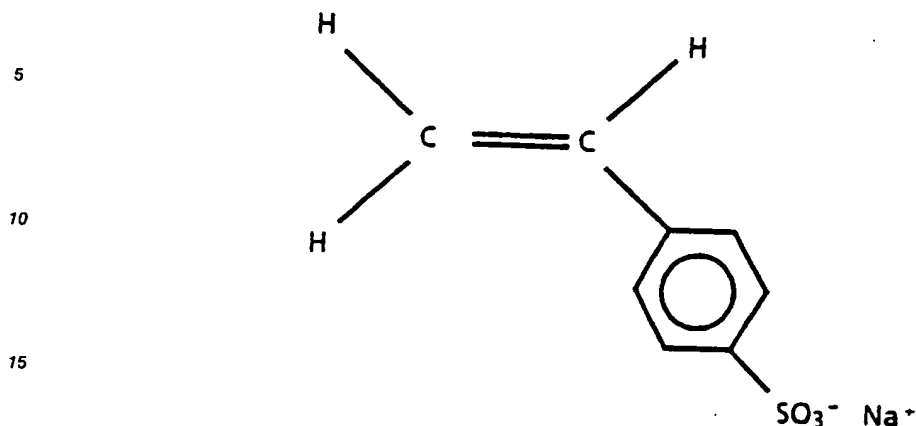
43. The process of claim 39 wherein the vinyl aromatic salt is of the formula



wherein R is an aromatic moiety with from 6 to 20 carbon atoms, X is an acid salt functional group
 consisting of both cation and anion moieties, and R₁, R₂ and R₃ are independently selected from the
 group consisting of hydrogen, alkyl groups with from 1 to 20 carbon atoms, aromatic groups with from
 6 to 20 carbon atoms, and heterocyclic groups.

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44. The process of claim 39 wherein the vinyl aromatic salt is of the formula



20 45. The process of claim 39 wherein the vinyl aromatic salt is a styrene sulfonate salt.

46. The process of claim 39 wherein the image on the substrate is electrically conductive.

25 47. The process of claim 39 wherein the substrate is plain paper and the image on the substrate has an optical density of from 1.0 to 1.45 optical density units.

48. The process of claim 39 wherein the substrate is silica coated paper and the image on the substrate has an optical density of from 1.2 to 1.78 optical density units.

30 49. The process of claim 39 wherein the image on the substrate exhibits waterfastness of greater than 95 percent, lightfastness of greater than 95 percent, and a resolution of at least 288 spots per 2.54 cm (inch).

35 **Patentansprüche**

1. Tintenzusammensetzung, welche eine wäßrige Trägerflüssigkeit und Pigmentpartikel mit einem auf ihren Oberflächen chemisch aufgepfropften polymerisierten vinylaromatischen Salz in Form eines Homopolymeren oder Copolymeren umfaßt.

40 2. Tintenzusammensetzung gemäß Anspruch 1, worin das Pigment Ruß ist.

3. Tintenzusammensetzung gemäß Anspruch 1, worin die Pigmentpartikel nicht-mutagene und nicht-toxische Rußpartikel mit einem Gehalt an polyaromatischen Kohlenwasserstoff von weniger als 1 ppm sind.

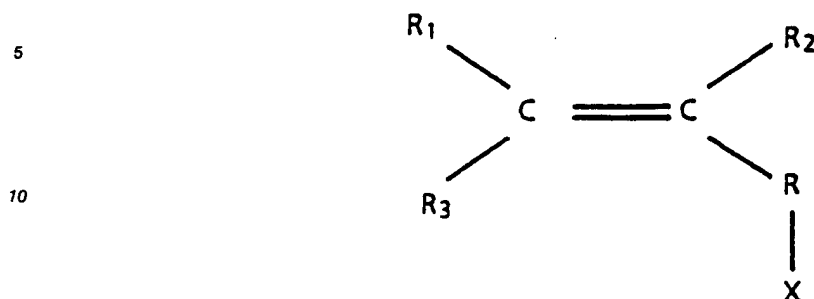
45 4. Tintenzusammensetzung gemäß Anspruch 1, worin das Pigment aus der aus Cyanpigmenten, Magentapigmenten, gelben Pigmenten, roten Pigmenten, blauen Pigmenten, grünen Pigmenten, orangen Pigmenten und deren Mischungen bestehenden Gruppe ausgewählt ist.

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5. Tintenzusammensetzung gemäß Anspruch 1, worin das vinylaromatische Salz die Formel



15
 aufweist, worin R ein aromatischer Rest, X eine funktionelle Säuresalzgruppe und R₁, R₂ und R₃ unabhängig voneinander ausgewählt sind aus der aus Wasserstoff, Alkylgruppen, substituierten Alkylgruppen, aromatischen Gruppen, substituierten aromatischen Gruppen, heterocyclischen Gruppen und substituierten heterocyclischen Gruppen bestehenden Gruppe.

- 20
 6. Tintenzusammensetzung gemäß Anspruch 1, worin die Trägerflüssigkeit Wasser und ein Feuchthaltemittel umfaßt.

25
 7. Tintenzusammensetzung gemäß Anspruch 6, worin das Feuchthaltemittel ausgewählt ist aus der aus Ethylenglykol, Propylenglykol, Diethylenglykole, Glycerin, Dipropylenglykole, Polyethylenglykole, Polypropylenglykole, Amide, Ether, Carbonsäuren, Ester, Alkohole, Organosulfide, Organosulfoxide, Sulfone, Alkoholderivate, Carbitol, Butylcarbitol, Cellulose, Etherderivate, Aminoalkohole, Ketone und deren Mischungen bestehenden Gruppe.

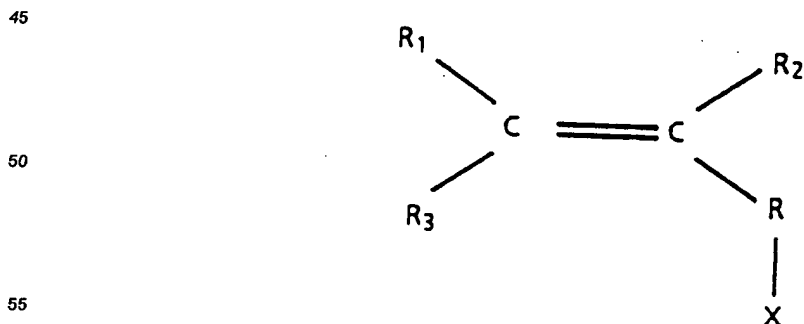
- 30
 8. Tintenzusammensetzung gemäß Anspruch 6, worin die Trägerflüssigkeit Wasser in einer Menge von 40 bis 100 Gew.-% und ein Feuchthaltemittel in einer Menge von 0 bis 60 Gew.-% umfaßt.

- 35
 9. Tintenzusammensetzung gemäß Anspruch 1, worin die Pigmentpartikel einen durchschnittlichen Partikeldurchmesser von 0,001 bis 10 µm aufweisen.

10. Tintenzusammensetzung gemäß Anspruch 1, worin die Pigmentpartikel einen durchschnittlichen Partikeldurchmesser von weniger als 1 µm aufweisen.

- 40
 11. Tintenzusammensetzung gemäß Anspruch 1, worin die Pigmentpartikel, die auf ihren Oberflächen ein chemisch aufgepfropft polymerisiertes vinylaromatisches Salz aufweisen, in der Tintenzusammensetzung in einer Menge von 0,1 bis 15 Gew.-% vorliegen.

12. Tintenzusammensetzung gemäß Anspruch 1, worin das vinylaromatische Salz die Formel

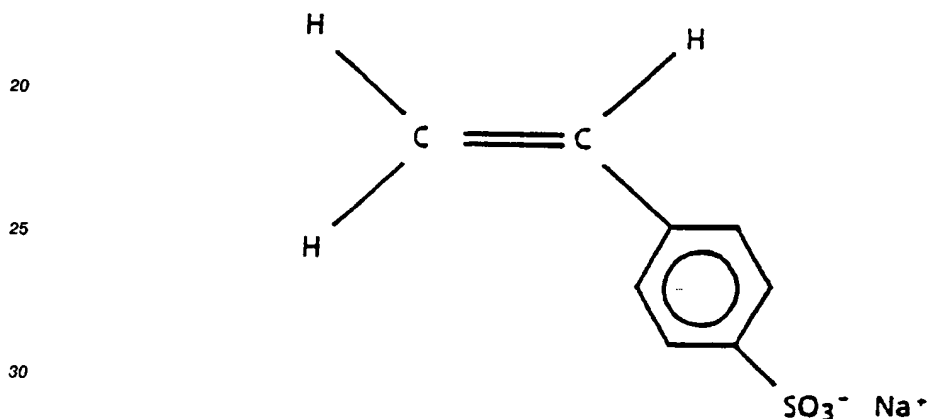


aufweist, worin R ein aromatischer Rest mit 6 bis 20 Kohlenstoffatomen ist, X eine funktionelle

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Säuresalzgruppe, bestehend sowohl aus kationischen als auch aus anionischen Resten ist, und R_1 , R_2 und R_3 unabhängig voneinander ausgewählt sind aus der aus Wasserstoff, Alkylgruppen mit 1 bis 20 Kohlenstoffatomen, aromatischen Gruppen mit 6 bis 20 Kohlenstoffatomen und heterocyclischen Gruppen bestehenden Gruppe.

- 5
13. Tintenzusammensetzung gemäß Anspruch 12, worin R ausgewählt ist aus der aus Phenyl, substituiertes Phenyl, Naphtyl, substituiertes Naphtyl, Anthracenyl, substituiertes Anthracenyl und heterocyclischen aromatischen Ringen bestehenden Gruppe.
- 10
14. Tintenzusammensetzung gemäß Anspruch 12, worin X eine funktionelle Salzgruppe ist, worin das Kation ausgewählt ist aus der aus Rb^+ , Cs^+ , K^+ , Na^+ , Li^+ , Ammonium und substituiertes Ammonium bestehenden Gruppe und das Anion ausgewählt ist aus der aus Sulfonat, Carboxylat, Phosphat und Borat bestehenden Gruppe.
- 15
15. Tintenzusammensetzung gemäß Anspruch 1, worin das vinylaromatische Salz die Formel

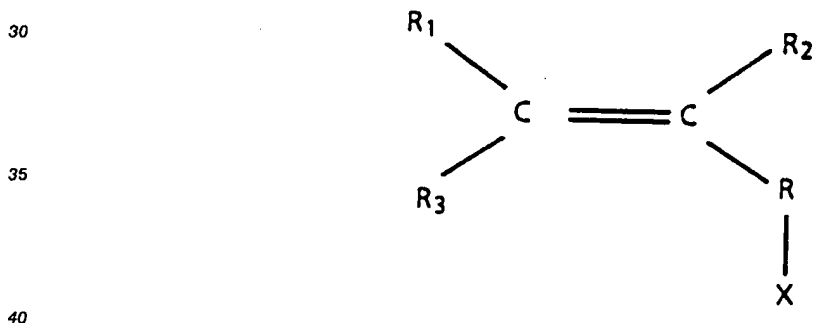


aufweist.

- 35
16. Tintenzusammensetzung gemäß Anspruch 1, worin das vinylaromatische Salz ein Styrolsulfonsäuresalz ist.
- 40
17. Tintenzusammensetzung gemäß Anspruch 1, welche auch einen Farbstoff enthält.
18. Tintenzusammensetzung gemäß Anspruch 17, worin der Farbstoff in einer Menge von nicht mehr als 15 Gew.-% vorliegt.
- 45
19. Tintenzusammensetzung gemäß Anspruch 1, welche ebenfalls ein Dispersionsmittel, ausgewählt aus der aus kationischen Dispersionsmitteln, anionischen Dispersionsmitteln und nicht-ionischen Dispersionsmitteln bestehenden Gruppe, enthält.
- 50
20. Tintenzusammensetzung gemäß Anspruch 19, worin das Dispersionsmittel in einer Menge von nicht mehr als 40 Gew.-% vorliegt.
21. Tintenzusammensetzung gemäß Anspruch 1, welche auch einen wasserlöslichen polymeren Zusatz enthält.
- 55
22. Tintenzusammensetzung gemäß Anspruch 21, worin der polymere Zusatz ausgewählt ist aus der aus Gummi arabicum, Polyacrylsäuresalzen, Polymethacrylsäuresalzen, Polyvinylalkoholen, Polyethylenoxiden, Polyethylenglykolen, Polypropylenglykolen, Hydroxypropylcellulose, Hydroxyethylcellulose, Polyvinylpyrrolidon, Polyvinylether, Stärke, Polyacrylamid, Ligninsulfonsäuresalzen, Copolymeren von Naphthalinsulfonsäuresalzen mit Formaldehyd und Polysacchariden bestehenden Gruppe.

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23. Tintenzusammensetzung gemäß Anspruch 21, worin der polymere Zusatz in einer Menge von 0,01 bis 5 Gew.-% vorliegt.
24. Verfahren zur Herstellung einer Tintenzusammensetzung welches umfaßt: Das Vermischen eines Pigmentes und eines vinylaromatischen Salzes in Wasser, Zerreiben der Mischung bis die Pigmentpartikel einen durchschnittlichen Partikeldurchmesser von 0,001 bis 20 µm haben, Hinzufügen eines wasserlöslichen, freie Radikale liefernden Polymerisationsinitiators zur Mischung und Erhitzen der Mischung unter Vakuum oder einer inerten Atmosphäre, wobei das vinylaromatische Salz polymerisiert und chemisch auf die Pigmentpartikel-Oberflächen gepfropft wird, Abtrennen der Pigmentpartikel von der Mischung und Zumischen der Pigmentpartikel zu einem flüssigen Träger.
25. Verfahren gemäß Anspruch 24, worin nachfolgend auf das Zumischen der Pigmentpartikel zu dem flüssigen Träger zur Entfernung von Pigmentpartikeln mit einem durchschnittlichen Partikeldurchmesser größer als 1 µm die Tintenzusammensetzung zentrifugiert und filtriert wird.
26. Verfahren gemäß Anspruch 24, worin die Polymerisation des monomeren vinylaromatischen Salzes bei einer Temperatur von 20 bis 120 °C durchgeführt wird.
27. Verfahren gemäß Anspruch 24, worin die Mischung aus Wasser, Pigment und monomeren vinylaromatischen Salz für einen Zeitraum von 0,25 bis 48 Stunden zerrieben wird.
28. Verfahren gemäß Anspruch 24, worin vor der Polymerisation die Mischung Wasser in einer Menge von 35 bis 98 Gew.-%, Pigmentpartikel in einer Menge von 2 bis 65 Gew.-%, monomeres vinylaromatisches Salz in einer Menge von 0,02 bis 50 Gew.-%, einen freie Radikale liefernden Polymerisationsinitiator in einer Menge von 0,01 bis 15 Gew.-% und ein Netzmittel in einer Menge von 0 bis 50 Gew.-% umfaßt.
29. Verfahren gemäß Anspruch 24, worin das vinylaromatische Salz die Formel



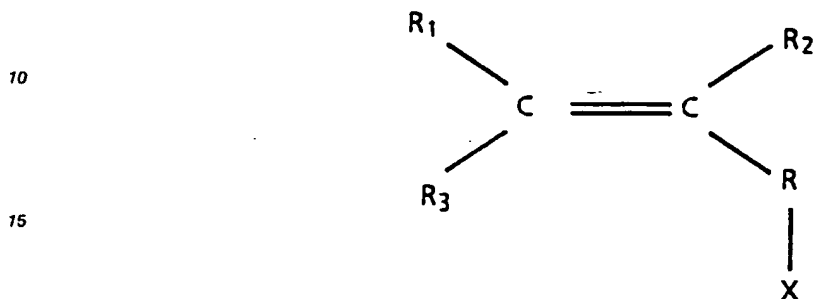
aufweist, in der R ein aromatischer Rest ist, X eine funktionelle Säuresalzgruppe ist und R₁, R₂ und R₃ unabhängig voneinander aus der aus Wasserstoff, Alkylgruppen, substituierten Alkylgruppen, aromatischen Gruppen, substituierten aromatischen Gruppen, heterocyclischen Gruppen und substituierten heterocyclischen Gruppen bestehenden Gruppe ausgewählt sind.

30. Verfahren gemäß Anspruch 29, worin R aus der aus Phenyl, substituiertes Phenyl, Naphthyl, substituiertes Naphthyl, Anthracenyl, substituiertes Anthracenyl und heterocyclischen aromatischen Ringen bestehenden Gruppe ausgewählt ist.
31. Verfahren gemäß Anspruch 24, worin die Pigmentpartikel, die auf ihren Oberflächen chemisch aufgepfropfte polymerisierte vinylaromatische Salze aufweisen, einen durchschnittlichen Partikeldurchmesser von 0,001 bis 10 µm haben.
32. Verfahren gemäß Anspruch 24, worin die Pigmentpartikel, die auf ihren Oberflächen chemisch aufgepfropfte polymerisierte vinylaromatische Salze aufweisen, einen durchschnittlichen Partikeldurchmesser von weniger als 1 µm haben.

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33. Verfahren gemäß Anspruch 24, worin die Pigmentpartikel, die auf ihren Oberflächen chemisch aufgefropfte polymerisierte vinylaromatische Salze aufweisen, in der Tintenzusammensetzung in einer Menge von 0,1 bis 15 Gew.-% vorliegen.

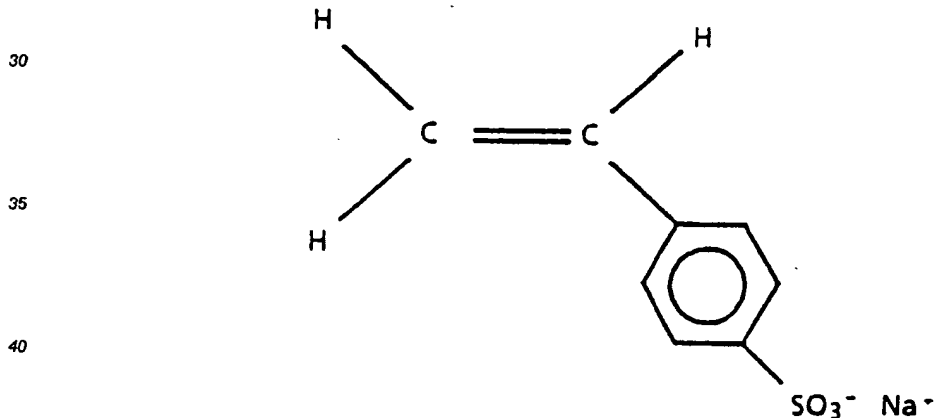
5 34. Verfahren gemäß Anspruch 24, worin das vinylaromatische Salz die Formel



20 aufweist, worin R ein aromatischer Rest mit 6 bis 20 Kohlenstoffatomen ist, X eine funktionelle Säuresalzgruppe, bestehend sowohl aus kationischen als auch aus anionischen Resten, und R₁, R₂ und R₃ unabhängig voneinander ausgewählt sind aus der aus Wasserstoff, Alkylgruppen mit 1 bis 20 Kohlenstoffatomen, aromatischen Gruppen mit 6 bis 20 Kohlenstoffatomen und heterocyclischen Gruppen bestehenden Gruppe.

25

35. Verfahren gemäß Anspruch 24, worin das vinylaromatische Salz die Formel



45

aufweist.

36. Verfahren gemäß Anspruch 24, worin das vinylaromatische Salz ein Styrolsulfonsäuresalz ist.

37. Verfahren zur Herstellung einer Tintenzusammensetzung, welches umfaßt:

50

a. Herstellung modifizierter Pigmentpartikel durch:

- 55
- i. Zuerst Zusammenmischen eines freie Radikale liefernden Polymerisationsinitiators und eines monomeren vinylaromatischen Salzes in Wasser und Erhitzen der Mischung unter Vakuum oder in einer inerten Atmosphäre, wobei das vinylaromatische Salz polymerisiert; und
 - ii. nachfolgend Zusatz von Pigmentpartikeln mit einem durchschnittlichen Partikeldurchmesser von 0,001 bis 10 µm zum polymerisierten vinylaromatischen Salz, zusätzlichen vinylaromatischen Salz-Monomeren und wahlweise ein freie Radikale liefernder Polymerisationsinitiator, hierdurch weitere Polymerisation des vinylaromatischen Salzes, resultierend in einem chemischen Aufpfropfen des polymerisierten vinylaromatischen Salzes auf den Oberflächen der Pigmentpartikel; und

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b. Zumischen der so hergestellten modifizierten Pigmentpartikel zu einem flüssigen Träger.

38. Verfahren zur Herstellung einer Tintenzusammensetzung, welches umfaßt:

a. Herstellung modifizierter Pigmentpartikel durch:

- 5 i. Zuerst Zusammenmischen von Pigmentpartikeln mit einem durchschnittlichen Partikeldurchmesser von 0,001 bis 10 µm, eines monomeren vinylaromatischen Salz und eines freie Radikale liefernder Polymerisationsinitiator in Wasser und Erhitzen der Mischung unter Vakuum oder in einer inerten Atmosphäre, wobei die vinylaromatischen Salze polymerisieren; und
- 10 ii. nachfolgend Zugabe von zusätzlichen vinylaromatischen Salz-Monomeren und wahlweise zusätzlich ein freie Radikale liefernder Polymerisationsinitiator, hierdurch weitere Polymerisation des vinylaromatischen Salzes, wobei das polymerisierte vinylaromatische Salz auf den Oberflächen der Pigmentpartikel chemisch aufgepfropft wird; und

b. Zumischen der so hergestellten modifizierten Pigmentpartikel zu einem flüssigen Träger.

- 15 **39. Verfahren zur Erzeugung von Bildern auf einem Substrat welches das Einbringen einer Tintenzusammensetzung in einen Tintenstrahldrucker umfaßt, welche eine wäßrige Trägerflüssigkeit und Pigmentpartikel mit einem auf ihren Oberflächen chemisch aufgepfropften polymerisierten vinylaromatischen Salz in der Form eines Homopolymeren oder eines Copolymeren umfaßt und Ausstoßen der Tröpfchen der Tintenzusammensetzung auf das Substrat verursacht.**

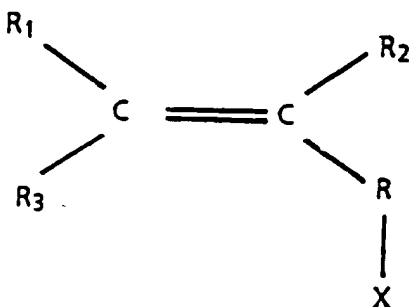
- 20 **40. Verfahren gemäß Anspruch 39, worin das Substrat aus der aus unbeschichteten Papier, Silika-beschichteten Papier, transparenten Material, Gewebe und Plastik bestehenden Gruppe ausgewählt ist.**

- 41. Verfahren gemäß Anspruch 39, worin der Tintenstrahldrucker ein thermischer Tintenstrahldrucker ist.**

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- 42. Verfahren gemäß Anspruch 39, worin das vinylaromatische Salz Monomere der Formel**

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aufweist, in der R ein aromatischer Rest ist, X eine funktionelle Säuresalzgruppe ist und R₁, R₂ und R₃ unabhängig voneinander aus der aus Wasserstoff, Alkylgruppen, substituierten Alkylgruppen, aromatischen Gruppen, substituierten aromatischen Gruppen, heterocyclischen Gruppen und substituierten heterocyclische Gruppen bestehende Gruppe ausgewählt sind.

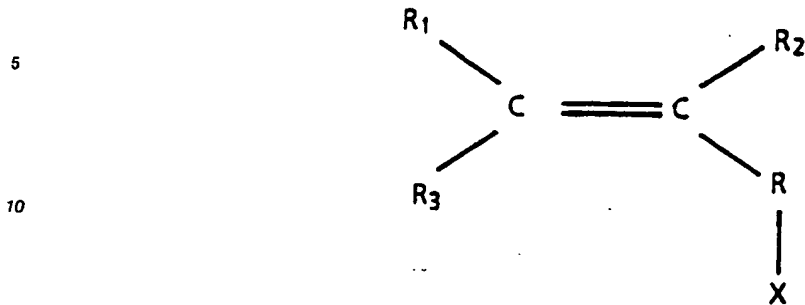
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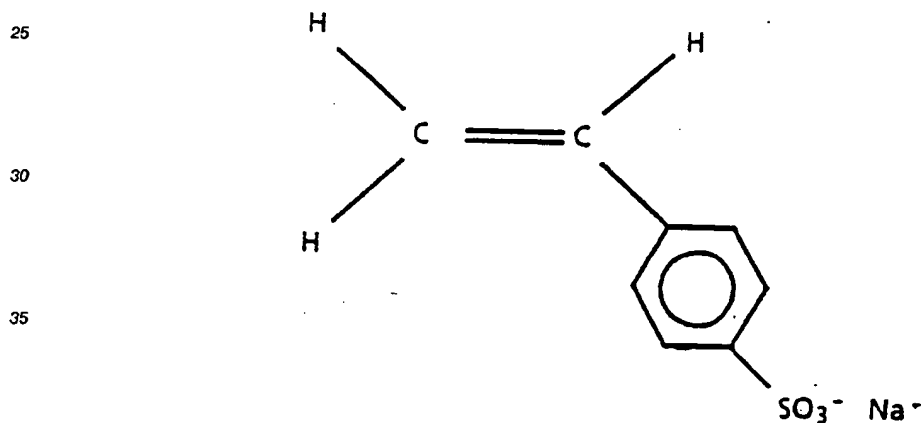
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43. Verfahren gemäß Anspruch 39, worin das vinylaromatische Salz die Formel



20 aufweist, worin R ein aromatischer Rest mit 6 bis 20 Kohlenstoffatomen ist, X eine funktionelle Säuresalzgruppe, bestehend sowohl aus kationischen als auch aus anionischen Resten, und R₁, R₂ und R₃ unabhängig voneinander ausgewählt sind aus der aus Wasserstoff, Alkylgruppen mit 1 bis 20 Kohlenstoffatomen, aromatischen Gruppen mit 6 bis 20 Kohlenstoffatomen und heterocyclischen Gruppen bestehenden Gruppe.

44. Verfahren gemäß Anspruch 39, worin das vinylaromatische Salz die Formel



aufweist.

45. Verfahren gemäß Anspruch 39, worin das vinylaromatische Salz ein Styrolsulfonsäuresalz ist.

46. Verfahren gemäß Anspruch 39, worin das Bild auf dem Substrat elektrisch leitend ist.

47. Verfahren gemäß Anspruch 39, worin das Substrat unbeschichtetes Papier und das Bild auf dem Substrat eine optische Dichte von 1,0 bis 1,45 optischen Dichteeinheiten aufweist.

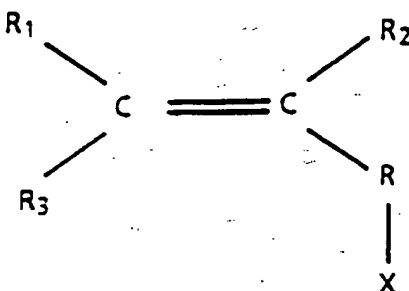
48. Verfahren gemäß Anspruch 39, worin das Substrat Silika-beschichtetes Papier ist und das Bild auf dem Substrat eine optische Dichte von 1,2 bis 1,78 optischen Dichteeinheiten aufweist.

49. Verfahren gemäß Anspruch 39, worin das Bild auf dem Substrat eine Wasserfestigkeit größer als 95 Prozent, eine Lichtechtheit größer als 95 Prozent und eine Auflösung von mindestens 288 Punkten pro 2,54 cm (inch) aufweist.

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Revendications

1. Composition d'encre comprenant un véhicule liquide aqueux et des particules de pigment ayant chimiquement greffé sur leurs surfaces un sel aromatique de vinyle polymérisé sous la forme d'un homopolymère ou d'un copolymère.
2. Composition d'encre selon la revendication 1, dans laquelle le pigment est du noir de carbone.
3. Composition d'encre selon la revendication 1, dans laquelle les particules de pigment sont des particules de noir de carbone non toxiques, non mutagènes, avec une teneur en hydrocarbure polyaromatique inférieure à 1 ppm.
4. Composition d'encre selon la revendication 1, dans laquelle le pigment est choisi dans le groupe constitué des pigments cyan, des pigments magenta, des pigments jaunes, des pigments rouges, des pigments bleus, des pigments verts, des pigments oranges, et de leurs mélanges.
5. Composition d'encre selon la revendication 1, dans laquelle le sel aromatique de vinyle répond à la formule :



dans laquelle R est une partie aromatique, X un groupe fonctionnel d'un sel d'acide, et R₁, R₂, et R₃ sont choisis indépendamment dans le groupe constitué d'un atome d'hydrogène, de groupes alkyle, de groupes alkyle substitués, de groupes aromatiques, de groupes aromatiques substitués, de groupes hétérocycliques, et de groupes hétérocycliques substitués.

6. Composition d'encre selon la revendication 1, dans laquelle le véhicule liquide comprend de l'eau et un agent d'humidification.
7. Composition d'encre selon la revendication 6, dans laquelle l'agent d'humidification est choisi dans le groupe constitué de l'éthylène glycol, du propylène glycol, de diéthylène glycols, de la glycérine, de dipropylène glycols, de polyéthylène glycols, de polypropylène glycols, d'amides, d'éthers, d'acides carboxyliques, d'esters, d'alcools, d'organosulfures, d'organosulfoxydes, de sulfones, de dérivés de l'alcool, du carbitol, du butyl carbitol, de la cellosolve, des dérivés d'éther, des amino alcools, des cétones, et de leurs mélanges.
8. Composition d'encre selon la revendication 6, dans laquelle le véhicule liquide comprend de l'eau dans une quantité de 40 à 100 pour cent en poids et un agent d'humidification dans une quantité de 0 à 60 pour cent en poids.
9. Composition d'encre selon la revendication 1, dans laquelle les particules de pigment ont un diamètre moyen ces particules compris entre 0,001 et 10 µm.
10. Composition d'encre selon la revendication 1, dans laquelle les particules de pigment ont un diamètre moyen des particules inférieur à 1 µm.
11. Composition d'encre selon la revendication 1, dans laquelle les particules de pigment ayant le sel aromatique de vinyle polymérisé greffé chimiquement sur leurs surfaces sont présentes dans la

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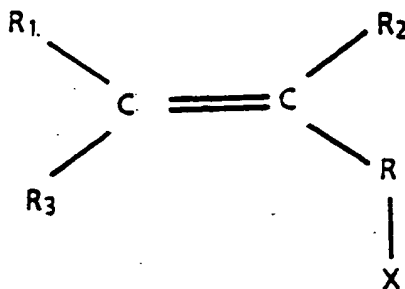
composition d'encre dans une quantité comprise entre 0,1 et 15 pour cent en poids.

12. Composition d'encre selon la revendication 1, dans laquelle le sel aromatique de vinyle répond à la formule :

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dans laquelle R est une partie aromatique avec 6 à 20 atomes de carbone, X est un groupe fonctionnel d'un sel d'acide constitué d'une partie cation et d'une partie anion, et R₁, R₂ et R₃ sont choisis indépendamment dans le groupe constitué d'un atome d'hydrogène, de groupes alkyle ayant 1 à 20 atomes de carbone, de groupes aromatiques ayant 6 à 20 atomes de carbone et de groupes hétérocycliques.

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13. Composition d'encre selon la revendication 12, dans laquelle R est choisi dans le groupe constitué des groupes phényle, phényle substitué, naphthyle, naphthyle substitué, anthracényle, anthracényle substitué, et des cycles aromatiques hétérocycliques.

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14. Composition d'encre selon la revendication 12, dans laquelle X est un groupe fonctionnel d'un sel dans lequel le cation est choisi dans le groupe constitué de Rb⁺, Cs⁺, K⁺, Na⁺, Li⁺, de l'ammonium et de l'ammonium substitué, et l'anion est choisi dans le groupe constitué d'un sulfonate, d'un carboxylate, d'un phosphate et d'un borate.

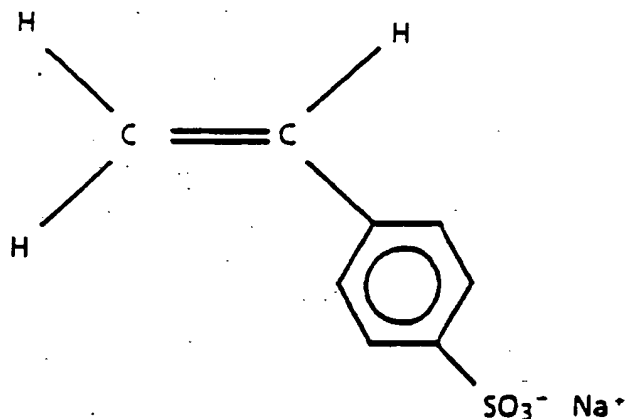
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15. Composition d'encre selon la revendication 1, dans laquelle le sel aromatique de vinyle répond à la formule :

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16. Composition d'encre selon la revendication 1, dans laquelle le sel aromatique de vinyle est un sel de sulfonate de styrène.

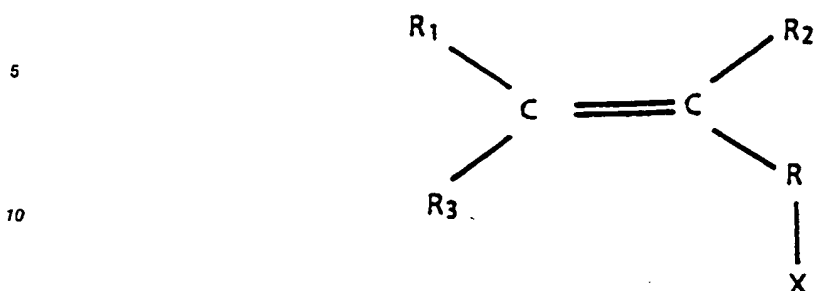
17. Composition d'encre selon la revendication 1, qui contient aussi un colorant.

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18. Composition d'encre selon la revendication 17, dans laquelle le colorant est présent dans une quantité non supérieure à 15 pour cent en poids.
19. Composition d'encre selon la revendication 1, qui contient aussi un agent de dispersion choisi dans le groupe constitué des agents de dispersion cationiques des agents de dispersion anioniques et des agents de dispersion non ioniques.
20. Composition d'encre selon la revendication 19, dans laquelle l'agent de dispersion est présent dans une quantité non supérieure à 40 pour cent en poids.
21. Composition d'encre selon la revendication 1, qui contient aussi un additif polymère soluble dans l'eau.
22. Composition d'encre selon la revendication 21, dans laquelle l'additif polymère est choisi dans le groupe constitué de : gomme arabique, sels de polyacrylate, sels de polyméthacrylate, alcools polyvinyliques, oxydes de polyéthylène, polyéthylène glycols, polypropylène glycols, hydroxypropylcellulose, hydroxyéthylcellulose, polyvinylpyrrolidinone, polyvinyléther, amidon, polyacrylamide, sels de sulfonate de lignine, copolymères de sels de sulfonate de naphthalène et formaldéhyde, et polysaccharides.
23. Composition d'encre selon la revendication 21, dans laquelle l'additif polymère est présent dans une quantité comprise entre 0,01 et 5 pour cent en poids.
24. Procédé pour préparer une composition d'encre qui comprend les étapes consistant à mélanger dans l'eau un pigment et un sel aromatique de vinyle, à soumettre à une attrition le mélange jusqu'à ce que les particules de pigment aient un diamètre moyen des particules compris entre 0,001 et 20 μm à ajouter au mélange un agent d'amorçage radicalaire de polymérisation soluble dans l'eau et à chauffer le mélange sous vide ou atmosphère inerte, d'où la polymérisation du sel aromatique de vinyle, et sa greffe chimique aux surfaces des particules du pigment, à séparer les particules du pigment du mélange, et à mélanger les particules du pigment à un véhicule liquide.
25. Procédé selon la revendication 24, dans lequel, à la suite du mélange des particules de pigment avec le véhicule liquide, la composition d'encre est soumise à une centrifugation et à un filtrage pour enlever les particules du pigment ayant un diamètre moyen des particules supérieur à 1 μm .
26. Procédé selon la revendication 24, dans lequel la polymérisation du sel aromatique de vinyle monomère est effectuée à une température comprise entre 20 et 120 °C.
27. Procédé selon la revendication 24, dans lequel le mélange d'eau, de pigment et de sel aromatique de vinyle monomère est soumis à une attrition pendant une durée de 0,25 à 48 heures.
28. Procédé selon la revendication 24, dans lequel, avant la polymérisation, le mélange comprend de l'eau dans une quantité de 35 à 98 pour cent en poids, des particules de pigment dans une quantité de 2 à 65 pour cent en poids, un sel aromatique de vinyle monomère dans une quantité de 0,02 à 50 pour cent en poids, un agent d'amorçage radicalaire de polymérisation dans une quantité de 0,01 à 15 pour cent en poids, et un agent mouillant dans une quantité de 0 à 50 pour cent en poids.

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29. Procédé selon la revendication 24, dans lequel le sel aromatique de vinyle répond à la formule :



15 dans laquelle R est une partie aromatique, X est un groupe fonctionnel d'un sel d'acide, et R₁, R₂ et R₃ sont choisis indépendamment dans le groupe constitué d'un atome d'hydrogène, de groupes alkyle, de groupes alkyle substitués, de groupes aromatiques, de groupes aromatiques substitués, de groupes hétérocycliques, et de groupes hétérocycliques substitués.

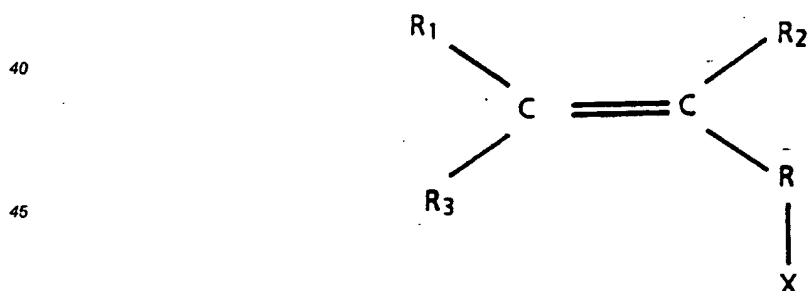
20 30. Procédé selon la revendication 29, dans lequel R est choisi dans le groupe constitué des groupes phényle, phényle substitué, naphthyle, naphthyle substitué, anthracényle, anthracényle substitué, et des cycles aromatiques hétérocycliques.

25 31. Procédé selon la revendication 24, dans lequel les particules de pigment, sur les surfaces desquelles sont greffés chimiquement les sels aromatiques de vinyle polymérisés ont un diamètre moyen des particules de 0,001 à 10 µm.

30 32. Procédé selon la revendication 24, dans lequel les particules de pigment, sur les surfaces desquelles sont greffés chimiquement les sels aromatiques de vinyle polymérisés ont un diamètre moyen des particules inférieur à 1 µm.

33. Procédé selon la revendication 24, dans lequel les particules de pigment, sur les surfaces desquelles sont greffés chimiquement les sels aromatiques de vinyle polymérisés sont présentes dans la composition d'encre suivant une quantité de 0,1 à 15 pour cent en poids.

34. Procédé selon la revendication 24, dans lequel le sel aromatique de vinyle répond à la formule :

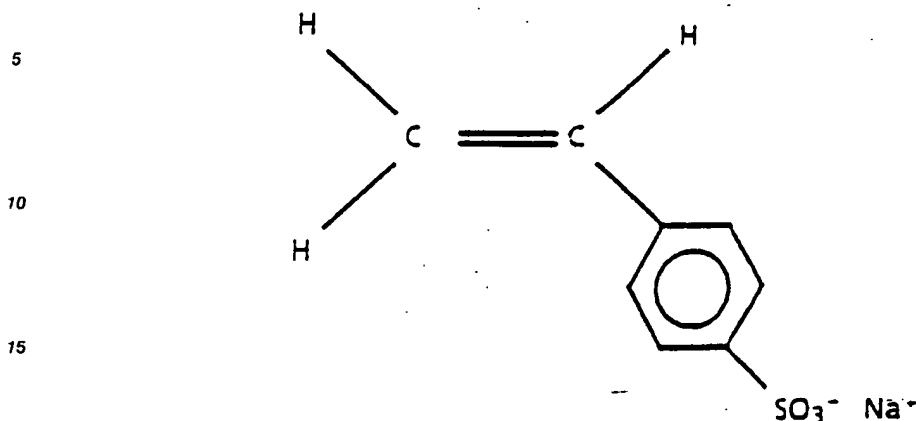


50 dans laquelle R est une partie aromatique ayant 6 à 20 atomes de carbone, X est un groupe fonctionnel d'un sel d'acide constitué de parties tant cation qu'anion, et R₁ et R₂ et R₃ sont choisis indépendamment dans le groupe constitué d'un atome d'hydrogène, de groupes alkyle ayant 1 à 20 atomes de carbone, de groupes aromatiques ayant 6 à 20 atomes de carbone et de groupes hétérocycliques.

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35. Procédé selon la revendication 24, dans lequel le sel aromatique de vinyle répond à la formule:



36. Procédé selon la revendication 24, dans lequel le sel aromatique de vinyle est un sel de sulfonate de styrène.

37. Procédé pour préparer une composition d'encre, qui comprend les étapes consistant à :

- 25 a. préparer des particules de pigment modifiées en :
- i. mélangeant tout d'abord ensemble dans de l'eau un agent d'amorçage radicalaire de polymérisation et un sel aromatique de vinyle monomère et chauffant le mélange sous vide ou atmosphère inerte, d'où la polymérisation du sel aromatique de vinyle; et
 - 30 ii. ajouter ensuite au sel aromatique de vinyle polymérisé des particules du pigment ayant un diamètre moyen des particules compris entre 0,001 et 10 µm, des monomères additionnels de sel aromatique de vinyle, et, en option, un agent d'amorçage radicalaire de polymérisation, d'où une nouvelle polymérisation du sel aromatique de vinyle et se traduisant par une greffe chimique du sel aromatique de vinyle polymérisé sur les surfaces des particules de pigment; et
 - b. mélanger les particules de pigment modifiées ainsi préparées avec un véhicule liquide.

38. Procédé pour préparer une composition d'encre qui comprend les étapes consistant à :

- 40 a. préparer des particules de pigment modifiées en :
- i. mélangeant d'abord ensemble dans de l'eau des particules de pigment ayant un diamètre moyen des particules compris entre 0,001 et 10 µm, un sel aromatique de vinyle monomère, et un agent d'amorçage radicalaire de polymérisation et chauffant le mélange sous vide ou atmosphère inerte, d'où la polymérisation des sels aromatiques de vinyle; et
 - 45 ii. ajouter ensuite au mélange des monomères additionnels de sel aromatique de vinyle, et, en option, un agent additionnel d'amorçage radicalaire de polymérisation, d'où une nouvelle polymérisation du sel aromatique de vinyle, où le sel aromatique de vinyle polymérisé est greffé chimiquement aux surfaces des particules de pigment; et
 - b. mélanger les particules de pigment modifiées ainsi préparées avec un véhicule liquide.

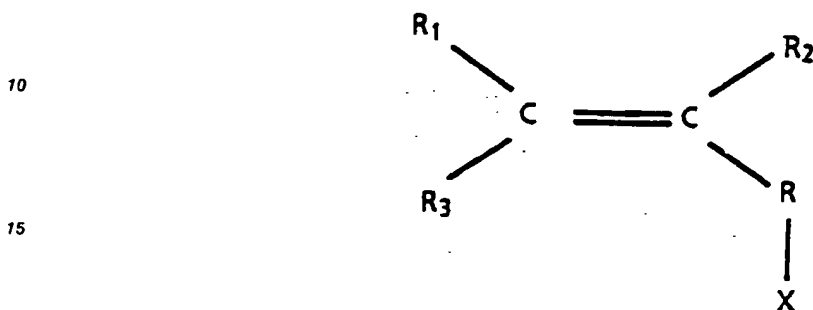
39. Procédé pour produire des images sur un substrat qui comprend l'incorporation dans un appareil d'impression à jet d'encre d'une composition d'encre comportant un véhicule liquide aqueux et des particules de pigment sur les surfaces desquelles est chimiquement greffé un sel aromatique de vinyle polymérisé sous forme d'un homopolymère ou d'un copolymère et amener les gouttelettes de la composition d'encre à être éjectées dans un motif en forme d'image sur le substrat.

40. Procédé selon la revendication 39, dans lequel le substrat est choisi dans le groupe constitué du papier ordinaire, du papier revêtu de silice, d'un matériau de transparence, d'un textile, et d'une matière plastique.

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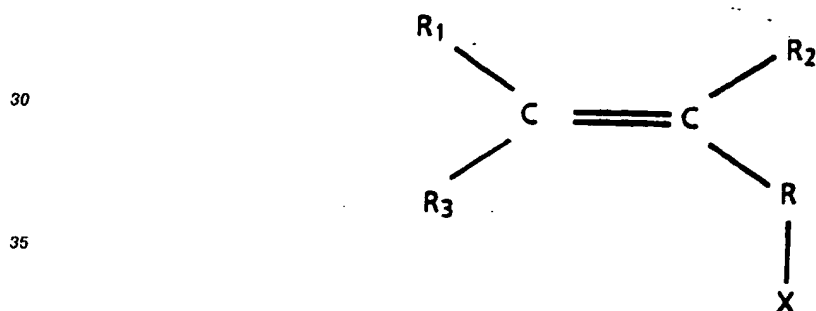
41. Procédé selon la revendication 39, dans lequel l'appareil d'impression à jet d'encre est une imprimante à jet d'encre thermique.

42. Procédé selon la revendication 39, dans lequel le sel aromatique de vinyle a des monomères répondant à la formule :



dans laquelle R est une partie aromatique, X est un groupe fonctionnel d'un sel d'acide, et R₁, R₂ et R₃ sont choisis indépendamment dans le groupe constitué d'un atome d'hydrogène, de groupes alkyle, de groupes alkyle substitués, de groupes aromatiques, de groupes aromatiques substitués, de groupes hétérocycliques, et de groupes hétérocycliques substitués.

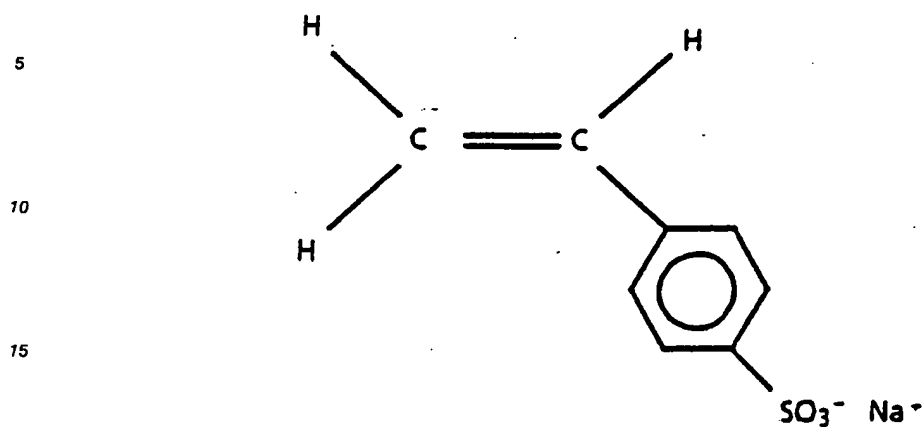
43. Procédé selon la revendication 39, dans lequel le sel aromatique de vinyle répond à la formule :



dans laquelle R est une partie aromatique ayant de 6 à 20 atomes de carbone, X est un groupe fonctionnel d'un sel d'acide constitué de parties cation et anion, et R₁, R₂ et R₃ sont choisis indépendamment dans le groupe constitué d'un atome d'hydrogène, de groupes alkyle ayant 1 à 20 atomes de carbone, de groupes aromatiques ayant de 6 à 20 atomes de carbone, et de groupes hétérocycliques.

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44. Procédé selon la revendication 39, dans lequel le sel aromatique de vinyle répond à la formule :



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45. Procédé selon la revendication 39, dans lequel le sel aromatique de vinyle est un sel de sulfonate de styrène.

46. Procédé selon la revendication 39, dans lequel l'image sur le substrat est conductrice de l'électricité.

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47. Procédé selon la revendication 39, dans lequel le substrat est du papier ordinaire et l'image sur le substrat a une densité optique comprise entre 1,0 et 1,45 unité de densité optique.

48. Procédé selon la revendication 39, dans lequel le substrat est du papier revêtu de silice et l'image sur le substrat a une densité optique comprise entre 1,2 et 1,78 unité de densité optique.

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49. Procédé selon la revendication 39, dans lequel l'image sur le substrat présente une solidité à l'eau supérieure à 95 pour cent, une solidité à la lumière supérieure à 95 pour cent, et une résolution d'au moins 288 points par 2,54 cm.

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